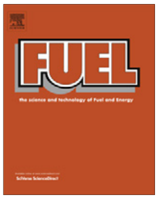
Fuel 107 (2013) 671–679

Contents lists available at SciVerse ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel



Impact of olefin content on criteria and toxic emissions from modern gasoline vehicles

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HIGHLIGHTS

- Changing the olefin content had a minor impact on exhaust emissions.
- Fuel olefin content had no statistically significant effect on NO_x, THC, NMHC, and CO emissions.
- Some fuel effects were observed for fuel economy and CO_2 emissions.
- 1,3-Butadiene emissions increased with increasing fuel olefin content.
- Benzene, formaldehyde, and acetaldehyde did not show statistically significant fuel effects.

ARTICLE INFO

Article history:
Received 7 September 2012
Received in revised form 6 December 2012
Accepted 6 December 2012
Available online 25 December 2012

Keywords:
Gasoline vehicles
Olefin content
Emissions
Carbonyls
1,3-Butadiene

ABSTRACT

Olefins are an important component of gasoline and an important property with respect to the development of reformulated gasolines using regulatory models. Currently, the coefficients used in regulatory gasoline development models are primarily based on studies conducted in the early 1990s, as an extensive study of olefin gasoline effects has not been conducted since that time. The goal of this study was to evaluate the impact of gasoline fuel olefin content on modern vehicles compliant with US EPA Tier 2 standards. Vehicles were tested with two fuels with different olefin contents, nominally 3% and 15% by volume, over the LA92 test cycle. The results showed that changing the olefin content with the range in this study had a relatively minor impact on exhaust emissions of these latest technology vehicles, including total hydrocarbons (THCs), nitrogen oxides (NO_x), and carbon monoxide (CO) emissions as well as toxic emissions such as formaldehyde, acetaldehyde, and benzene. Only exhaust 1,3-butadiene emissions showed significantly higher emissions at higher olefin levels, consistent with a correlation between olefins in the fuel and in the exhaust. This information from this study will be used to provide updates of fuel properties effects for use in the EPA Complex Model and the CARB Predictive Model.

1. Introduction

In an effort to improve ambient air quality in urban areas, the United States (US) and other countries throughout the world have implemented a number of regulations over the past several decades [1,2]. The US Environmental Protection Agency (EPA), as a part of its efforts to implement the Clean Air Act, has mandated the use of reformulated gasoline in nonattainment regions in the United States [3]. Federal and California regulations utilize models or sets of equations (i.e., the Complex Model (EPA) and the Predictive Model (California Air Resources Board-CARB) that describe the impact of fuel properties and composition on emissions and are used to develop and evaluate these reformulated gasolines [4,5]. These models are used by refiners to determine if the gasoline they are producing meets the emissions performance standards under the EPA's reformulated gasoline (RFG) program [5–7]. A number of studies were conducted in the early 1990s, including the Auto/Oil Air Quality Improvement Research Program (AQIRP) and studies by the EPA, to provide the initial basis for these models [8–13]. The Energy Policy Act of 2005 requires that EPA update the Complex Model to reflect the latest information on fuel and vehicle effects. This has provided the emphasis for a number of collaborative programs between the EPA, the Department of Energy (DOE), and the Coordinating Research Council (CRC) in recent years [14,15].

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0016-2361/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.fuel.2012.12.031

One of the major components of gasoline are olefins (alkenes), along with a mixture of other hydrocarbons, including paraffins (alkanes), naphthenes (cycloalkanes), and aromatics, and oxygenates [16]. Olefins are hydrocarbon compounds with one or more carbon double bonds. Olefins can increase the reactivity of gasoline fuels in combustion processes [17], and also improve fuel octane number and anti-knock performance [16,18,19]. However, high olefin content fuels have some disadvantages, such as higher olefin content exhaust emissions that have a higher ozone formation potential (OFP) [17], and also an increased tendency to form deposits in engine injectors and intake valves [16]. Reducing the olefin content of a fuel and substituting with paraffins reduces the reactivity of the fuel, which can lead to a less complete combustion. It has also been shown that reducing olefin content decreases the emissions of 1,3-butadiene, which is photo-reactive and contributes to photochemical smog [18].

Olefin content was one of the main fuel parameters evaluated in the AQIRP and EPA studies in the early 1990s [8–11,13,17]. These earlier studies showed that the impacts of olefins on the combustion process lead to measureable differences in exhaust emissions for vehicles of this earlier generation [8–11,13,17]. In the AQIRP program, reducing olefins from 20% to 5% was found to increase hydrocarbons emissions by 5.8 ± 2.0% and reduce NO_x emissions by 6.1 ± 1.9% in a fleet of 1989 vehicles, and to increase hydrocarbon emissions by 5.7 ± 3.0% and reduce NO_x by 6.7 ± 1.9% in a fleet of 1983–1985 vehicles [8]. EPA studies of this time showed similar trends of lower NO_x emissions with lower olefin content, but they did not see any impact of olefins on hydrocarbon emissions [11]. Studies of the impact of olefin content on modern vehicles exhaust emissions are fewer and less comprehensive, and have generally shown less consistent trends [17,20–23]. Additionally, while recent studies, such as those by CRC and EPA, have more extensively evaluated the emissions impacts of fuel properties such as sulfur content, T_{50}, T_{90}, ethanol content, aromatics content, and Reid Vapor Pressure (RVP) in modern vehicles [14,15,17], the impact of olefin content on exhaust emissions has not been extensively studied since the early 1990s.

The goal of this study is to provide a more comprehensive evaluation of the effect of olefin content on the exhaust emissions from the latest technology gasoline vehicles. In this study, the impact of olefin content on regulated and toxic exhaust emissions was evaluated for fifteen 2008 model year vehicles compliant with Tier 2 emissions standard regulations. Vehicles were tested with two fuels with different olefin contents, nominally 3% and 15% by volume, while being operated over the LA92 test cycle. Statistical analyses were then conducted to determine the significance of any observed fuel trends. This study is part of the larger series of studies by CRC, EPA, and DOE to evaluate fuel property impacts in modern vehicles [14,15]. This information will be used to provide updates of fuel properties effects for use in the EPA Complex Model and the CARB Predictive Model [24].

2. Experimental

2.1. Test fuels

Two gasoline fuels, denoted A and B, with different olefin content (nominally 3% and 15% in volume) were tested. The olefins levels were chosen so as to span the 10th and 90th percentile of US fuels based on survey data at the time the study was being planned. Except for olefin content, other fuel properties were designed to be equivalent within the specified ranges. Table 1 summarizes the selected fuel properties. These fuels were specially blended from standard refinery gasoline blending streams with a detergent additive, but without using any special chemicals or chemical blendstocks. Prior to testing, the engine oil was changed and the vehicles were conditioned for 2000 miles on a mileage accumulation dynamometer using the Standard Road Cycle.

2.2. Test vehicles

Fifteen 2008 Tier 2 USA EPA vehicles, eight passenger cars and seven light-duty trucks, were tested. The characteristics of the vehicles are provided in Table 2. All of these vehicles had been used in a recently completed, congressionally-mandated study jointly sponsored by EPA, DOE and CRC to measure the effects of changes in selected fuel properties on light-duty vehicle exhaust emissions [25]. All vehicles were equipped with three way catalyst (TWC) and exhaust gas recirculation (EGR) technology with heated oxygen (HO_2) sensor.

2.3. Driving cycle and test matrix

A test matrix with fully randomized order of test fuels for every test vehicle was used. The randomization of fuels A and B for every vehicle could be sequenced as AABB, ABBA, ABAB, or variations on these sequences. The randomization sequence for each vehicle is provided in Table S-1 in the Supporting information. The test cycle used in this program was the LA92 (also known as Unified) Cycle which is shown in Fig. S-1 in the Supporting information.

At least two replicates were performed on every vehicle/fuel combination. After the completion of two LA92 tests on each vehicle/fuel combination, the data was evaluated to determine if additional testing is required. A third test was performed if differences in LA92 regulated emissions exceeded a predefined limit using the criteria that were developed by Painter and Rutherford [26] and have been used in previous studies [27,28]. A third test was performed if the difference in the measurements exceeded the following: THC 33%, NO_x 29%, CO 70%. Since the emissions levels of modern vehicles are considerably lower than those for vehicles at the time these criteria were developed, this criteria was only applied if the absolute difference in the measurements was greater than 5 mg/mi. Based on these limits, triplicate tests were required on 13 of the 30 vehicle combinations. This is more than the number of replicates required in previous similar studies [27,28], which could be attributed to the more aggressive nature of the LA92 cycle compared to the Federal Testing Procedure (FTP). The emissions measurements for the third test included both regulated and toxic emissions.

2.4. Fuel conditioning

Before testing a vehicle/fuel combination, the vehicle was preconditioned on a new fuel with a procedure that included a fuel drain and fill (40%), followed by a catalyst sulfur purge cycle and four coast downs (70–30 mph). For the catalyst sulfur purge cycle, the inlet catalyst temperature and the exhaust A/F ratio were monitored with an OBDPRO serial scantool that was connected to the engine control unit (ECU). Either one or two additional drain and fills were done on each vehicle. The need for two additional drain and fills for some vehicles was based on the information obtained in the E-89/V2/EPACT program [25]. The vehicles requiring an extra drain and fill are identified in Table 2. The vehicle was then preconditioned over a single iteration of bags 1 and 2 of the LA-92 cycle on the dynamometer before the actual emissions test was conducted. An additional 15 min drive at 50 mph was conducted when the first fuel was tested on each vehicle to help condition the vehicle for the program. This sequence is shown schematically in Fig. S-2 in the Supporting information.

Following the initial emissions test, the vehicle was either placed into cold soak if the next test is on the same fuel or it under-