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Antiknock quality and ignition kinetics of 2-phenylethanol, a novel lignocellulosic octane booster

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Abstract

High-octane quality fuels are important for increasing spark ignition engine efficiency, but their production comes at a substantial economic and environmental cost. The possibility of producing high anti-knock quality gasoline by blending high-octane bio-derived components with low octane naphtha streams is attractive. 2-phenyl ethanol (2-PE), is one such potential candidate that can be derived from lignin, a biomass component made of interconnected aromatic groups. We first ascertained the blending anti-knock quality of 2-PE by studying the effect of spark advancement on knock for various blends 2-PE, toluene, and ethanol with naphtha in a cooperative fuels research engine. The blending octane quality of 2-PE indicated an anti-knock behavior similar or slightly greater than that of toluene, and ethylbenzene, which could be attributed to either chemical kinetics or charge cooling effects. To isolate chemical kinetic effects, a model for 2-PE auto-ignition was developed and validated using ignition delay times measured in a high-pressure shock tube. Simulated ignition delay times of 2-PE were also compared to those of traditional high-octane gasoline blending components to show that the gas phase reactivity of 2-PE is lower than ethanol, and comparable to toluene, and ethylbenzene at RON, and MON relevant conditions. The gas-phase reactivity of 2-PE is largely controlled by its aromatic ring, while the effect of the hydroxyl group is minimal. The higher blending octane quality of 2-PE compared to toluene, and ethylbenzene can be attributed primarily to the effect of the hydroxyl group on increasing heat of vaporization.

Keywords: Future fuel; Octane index

1. Introduction

The anti-knock quality of a fuel is of vital importance to spark ignition engine operation. Each year billions of dollars are spent on upgrading gasoline fuels to sufficiently high octane numbers, and this effort is set to continue as future spark

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ignition will demand even higher octane quality to meet ever stringent CO_2 emission regulations. The efforts to understand and prevent knock started in the early 20th century. Over the years, many compounds have been tested for anti-knock potential and few have made it to commercial use. The most infamous of these is tetraethyl lead (TEL) which was discontinued in 1996 due to its adverse health effects and the advent of catalytic converters [1]. Methyl tert-butyl ether (MTBE) is another effective anti-knock additive that has fallen out of favor as it was found to cause ground water contamination. The enhancement of octane rating is presently achieved by blending in iso-paraffins, aromatics, and oxygenates in the form of ethanol, and MTBE in certain countries.

Aromatics derived by reforming naphthenes play a major part in boosting the octane number, lowering the vapor pressure, and increasing the specific gravity of gasoline. However, the production of reformate is quite energy intensive and the presence of carcinogenic compounds like benzene raises health concerns. The synthesis of aromatic compounds required for gasoline blending from sustainably harvested lignin, a plant derived aromatic polymer [2], is attractive for environmental reasons. Nevertheless, there are numerous challenges to be conquered for industrializing aromatic production from lignin with the economic feasibility of upgrading bio-oil derived from fast pyrolysis of lignin being a major one [3]. The removal of oxygen in the upgrading process through hydro processing is a significant cost barrier. The possibility of using oxygenated aromatics as blending components into a low-octane gasoline (i.e., naphtha) can relieve part of the economic burden.

One such possible compound that can be obtained from lignin [3], and glucose [4] is 2-Phenylethanol (2-PE). This compound has a rose like smell, and mainly used as a flavoring and fragrance agent [5,6]. It has been investigated as a potential additive to diesel fuels [7], and also as a fuel for spark ignition engines [8]. Some important properties of 2-PE are compared with those of traditional high-octane gasoline blending components in Table 1. 2-PE has a higher heat of vaporization compared to other aromatics and a higher heating value compared to ethanol. The calculated RON (Research Octane Number) and MON (Motor Octane Number) of 2-PE [7] indicate high sensitivity, a quality that is desirable in downsized, highly boosted gasoline engines [9,10].

The goal of this study is to ascertain the suitability of 2-PE as an octane booster for low octane refinery streams, such as straight run naphtha. The study presents the relative blending anti-knock quality of 2-PE with respect to toluene (Tol), ethylbenzene (EB), and ethanol (EtOH) when blended with a low octane naphtha fuel and measured by knock limited spark advance (KLSA) tests performed in a modified cooperative fuels research (CFR) engine. A chemical kinetic model was developed to provide chemical evidence of 2-PE's reactivity and blending octane quality. The model was validated against ignition delay times measured in a high pressure shock tube (HPST). The gas phase reactivity is then compared with other octane enhancers and the results discussed.

2. Methodologies

2.1. CFR engine measurements

KLSA measurements were performed in a modified CFR engine to compare the blending anti-knock quality of 2-PE mixed with a low octane naphtha fuel, FACE I (Fuels for Advanced Combustion Engines). Initially, five fuels 1) FACE I, 2) FACE I + 10% 2-PE + 5% Tol, 3) FACE I + 15% Tol, 4) FACE I + 15% Ethylbenzene, and 5) FACE I + 15% EtOH were tested with an inlet air temperature of 302 ± 2 K, a close approximation to RON conditions. Four more blends, 1) FACE I + 20% 2-PE + 10% Tol, 2) FACE I + 30% Tol, 3) FACE I + 30% EB, and 4) FACE I + 30% EtOH were tested with at an elevated inlet air temperature of 378 ± 2 K, an approximation of MON conditions. The blending percentages stated above are volumetric, and toluene was required as a co-solvent to blend 2-PE with FACE I.

FACE I is a highly paraffinic research grade fuel with a RON of 70 and very little sensitivity formulated by the Coordinating Research Council, Inc. (CRC) [14]. It was chosen as the base stock because it is representative of low octane refinery streams. The engine was operated at a constant speed of 600 rpm, compression ratio of 6,

Table 1
Properties of 2-PE compared with other high octane components in gasoline.

	p-Xylene	Ethylbenzene	Toluene	2-PE	Ethanol
Molecular Formula	C8H10	C8H10	C7H8	C8H10O	C2H6O
RON	116.4[11]	107[12]	120[13]	110[7]	108[13]
Sensitivity	7.4[11]	9.5[12]	12[13]	20[7]	9[13]
Density at 300 K [kg/l]	0.857	0.867	0.866	1.017	0.784
Molar mass [kg/mol]	0.106	0.106	0.092	0.122	0.046
LHV [MJ/kg]	40.8	41.3	40.6	36.7	26.7
Heat of Vaporization [kJ/kg]	395.85	452.83	404.83	564.81	918.20

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