

Experimental and theoretical study of oxidative stability of alkylated furans used as gasoline blend components

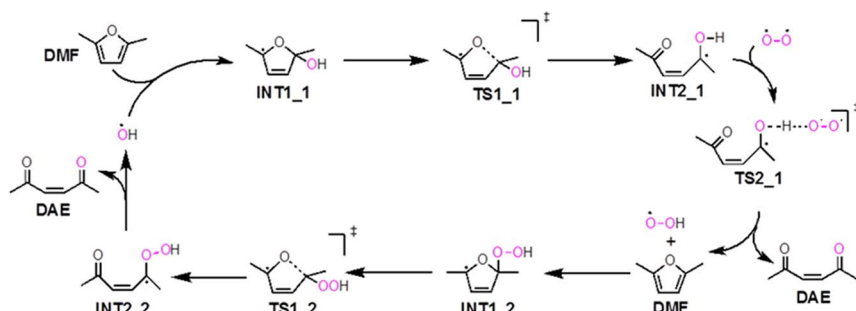


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GRAPHICAL ABSTRACT



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ABSTRACT

Alkylated furans such as 2,5-dimethylfuran and 2-methylfuran can be produced from biomass and have very attractive properties for use as spark-ignition fuel blendstocks. Their high octane numbers, relatively high energy density, low water solubility, and minimal effect on gasoline blend volatility are potentially significant advantages over alcohol-based fuels. However, prior studies have reported poor oxidative stability for furanic compound-gasoline blends, as well as the potential for the formation of dangerous organic peroxides. We show that alkylated furans have very low oxidative stability compared to conventional gasoline. Upon oxidation they form highly polar ring-opening products that can react with the starting furanic compound to form dimers, trimers, and higher polymers with intact furan rings. Dimers of the starting furan compounds were also observed. These gasoline-insoluble gums can be problematic for fuel storage or in vehicle fuel systems. Evaporation to dryness under ambient conditions also produced gum with similar composition. Gums produced via evaporation were found to contain peroxides; however, whether these pose a threat of shock initiated explosion has not been determined. We also propose a density functional theory-based analysis of possible reaction pathways, showing that OH radicals can form by reaction of the alkyl group and that addition of OH radicals to the furan ring is energetically favored and leads to ring opening products. Antioxidant additives can be effective at limiting the oxidation reaction in gasoline, but require much higher concentrations than are commonly used in commercial gasolines.

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1. Introduction

Furanic compounds, specifically 2,5-dimethylfuran (DMF) and 2-methylfuran (MF), have long been of interest as potential biofuels. Their boiling point, high octane number, relatively high heating value, low solubility in water, and minimal effect on gasoline blend volatility make them very attractive as components of fuels for spark-ignition engines (Table 1) [1,2]. It is particularly notable that these compounds exhibit very high blending octane numbers when blended into petroleum blendstocks, making them among the most attractive proposed biofuels for enabling the design and production of spark-ignition engines with significantly improved efficiency [2]. These compounds can be produced from lignocellulosic biomass via several different routes [3–8]. In one approach, DMF is produced from the C6 sugar fructose by dehydration to form hydroxymethylfurfural, which is then hydrogenated. Production from cellulose (a polymer of glucose), therefore, requires initial isomerization of glucose to fructose. MF can be produced from the C5 sugar xylose by dehydration to furfural followed by hydrogenation. A practical process for conversion of lignocellulosic biomass containing both cellulose and hemicellulose (a polymer of xylose) would produce a mixture of DMF and MF [9,10]. The combustion of DMF and MF has also been extensively studied theoretically [11,12], in fundamental experiments [13–15], and in engine combustion experiments [16–21].

Only a few studies have examined how these promising high-octane number compounds affect practical fuel properties when blended with conventional petroleum-derived gasoline blendstocks. Christensen and coworkers blended DMF and MF into a petroleum-derived hydrocarbon gasoline blendstock intended for blending with 10 vol% ethanol [1]. Blending of MF (11 percent by volume (vol%)) and DMF (13 vol%) showed little effect on vapor pressure and a 5–10 °C depression in the 50% evaporation temperature (T50) with no significant effect on T10 or T90, all very desirable properties for gasoline blending. Blends were very stable in the presence of water with no phase separation or uptake of oxygenate by the water phase. Very high volumetric blending research octane numbers of about 150 were observed at this blend level in the 85 research octane number blendstock.

Researchers at Shell Global Solutions conducted a detailed evaluation of MF as a gasoline component, reporting similar fuel property effects to those described above [23]. They also noted that MF blending degraded the oxidation stability of the fuel as measured by ISO 6246 (a standard test for measuring the oxidation stability and gum formation for gasoline), and furthermore noted increased inlet valve and injector deposits in a three-car, 90,000-km on-road test. In a previous study we reported that DMF blending can negatively impact gasoline stability, producing high levels of insoluble gum on the ASTM International (ASTM) D873 gum formation test for blends as low as 10 vol%, and failing the ASTM D525 oxidation stability test for a 20 vol% blend [24]. These standard stability tests are conducted at 100 °C under 700 kPa initial pressure of oxygen.

Additionally, Fabos and coworkers examined the formation of peroxides during storage of bio-derived oxygenates including DMF and

found that this compound increases in peroxide number over time similar to tetrahydrofuran (THF), which is a known peroxide former [25]. Interestingly, furan did not form high levels of peroxides. The formation of peroxides via oxidation at ambient conditions is a considerable safety concern as some organic peroxides can present an explosion hazard when exposed to physical shock. Many common laboratory solvents are known to form peroxides, and precautions are recommended that allow for their safe storage and handling. These precautions include protection from light and air, the use of free radical scavenging additives, as well as periodic monitoring for peroxide formation [26]. Petroleum-derived gasolines containing olefins are also known to form peroxides during storage, which degrades octane ratings and, if sufficient oxidation occurs, gums can form causing filter plugging and engine deposits [27]. Prevention of oxidation during fuel storage is vital for maintaining fuel quality.

Here we describe the results of an experimental and theoretical study examining the oxidation stability of furanic compounds within the contexts of both gasoline stability and peroxide formation as a safety issue.

2. Methods

2.1. Experimental

Furan, MF, DMF, and 2-ethylfuran (EF) with purity $\geq 99\%$ were purchased from Sigma Aldrich. Furan and MF were received containing 250 ppm (ppm) butylated hydroxytoluene stabilizer. DMF and EF were purchased without added stabilizers. Each compound was passed over a bed of silica to remove oxidation products, stabilizers, and other polar materials before use. DMF and MF as received exhibited a yellow color, which was removed by the silica resulting in a clear liquid. Blends for testing were prepared gravimetrically with 2,2,4-trimethylpentane (isooctane, purchased from VWR) to 10 vol% concentration.

Oxidation stability of blends was assessed at 100 °C under an initial pressure (at room temperature) of 700 kPa of oxygen. These are the test conditions of the ASTM D525 test used to measure the oxidation induction time (or breakpoint) of commercial gasolines. The test is run for 24 h while the pressure of the vessel is monitored for a breakpoint defined by a rate of pressure decrease of greater than 14 kPa per 15 min, which defines the induction period of the sample. A minimum induction time of 240 min is required for commercial gasoline in the United States. The final pressure at 24 h is reported, and the liquid phase is recovered for analysis. A gasoline gum formation test, ASTM D873, is conducted in the same apparatus at the same conditions for a fixed period of time – 24 h was used in this study. This is followed by solvent rinsing (50:50 by volume mixture of toluene and acetone), evaporation, and weighing of gum formed during oxidation.

In some cases, the DMF blend was treated with a mixture of proprietary antioxidants at the concentrations recommended by the manufacturer for effective gasoline stabilization. The antioxidant mixture contained phenylenediamine-based and hindered-phenol based components that were added to a 10 vol% DMF blend at concentrations of 10 and 30 ppm, respectively. An additional 10 vol% DMF blend was tested with 10 times the recommended concentration of these antioxidants (100 and 300 ppm).

Gum and peroxide formation at room temperature during furanic compound evaporation was assessed by allowing 100 mL of neat MF and DMF to evaporate in 250-mL Erlenmeyer flasks in a fume hood. Peroxides were measured following a modified version of ASTM method D3703 for peroxide number of gasoline, jet fuel, and diesel. This method was modified for potentiometric endpoint detection rather than colorimetric titration. The method has been modified for the use of potentiometric end point detection in the place of colorimetric titration to provide improved precision and throughput via use of an instrument based endpoint opposed to human eye detection of color change. Accuracy of the method with this modification was verified by

Table 1
Important fuel properties of DMF and MF.

Property	DMF	MF
Boiling point, °C	94	65
Research octane number [22]	101	103
Motor octane number [22]	88	86
Molar blending research octane number [1] ¹	137	131
Molar blending motor octane number [1]	102	101
Lower heating value, MJ/L	30.1	27.6
Water solubility, mg/L	1460	3410

¹ Molar blending octane numbers are for 11.3 vol% MF or 13.4 vol% DMF in a sub-octane gasoline blendstock, as described in more detail in Ref. [1].

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