

EFFECTS OF POTENTIAL ADDITIVES TO PROMOTE SEAL SWELLING ON THE THERMAL STABILITY OF SYNTHETIC JET FUELS

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Abstract

Synthetic fuels derived from the Fischer-Tropsch (F-T) process using natural gas or coal-derived synthesis gas as feedstocks can be used for powering of ground vehicles, aircraft and ships. Because of their chemical and physical properties, F-T fuels will probably require additives in order to meet specifications with respect to lubricity and seal swell capability for use in ground and air vehicles. These additives can include oxygenates and compounds containing other heteroatoms that may adversely affect thermal stability. In order to understand what additives will be the most beneficial, a comprehensive experimental and computational study of conventional and additized fuels has been undertaken. The experimental approach includes analysis of the trace oxygenate and nitrogen-containing compounds present in conventional petroleum-derived fuels and trying to relate their presence (or absence) to changes in the desired properties of the fuels. This paper describes the results of efforts to test the thermal stability of synthetic fuels and surrogate fuels containing single-component additives that have been identified in earlier research as the best potential additives for promoting seal swelling in synthetic fuels, as well as mixtures of synthetic and petroleum-derived fuels.

Keywords: jet fuel, thermal stability, Fischer-Tropsch, synthetic fuel, swelling, additives, benzyl alcohol

Introduction

Liquid fuels derived from non-traditional sources, such as the Fischer-Tropsch (F-T) process, continue to generate significant interest. Drivers include energy supply and energy security issues, as well as environmental benefits that are possible due to the clean burning characteristics of F-T fuels. F-T fuels are typically highly pure mixtures of paraffinic species, and they have an inherently high thermal stability, which is advantageous for applications where the circulating fuel is used as a heat sink to cool aircraft avionics. There are, however, significant roadblocks to the widespread implementation of these ultra-clean liquid fuels into the transportation and military sectors. These fuels fail to induce the same degree of swelling of traditional elastomeric materials that is observed when petroleum-derived fuels are used in current and legacy fleets of vehicles and aircraft.

The seal swell issue is critical. Some studies have proposed that the addition of aromatic species to synthetic fuels can induce seal swell¹. It has also been accepted that blending of petroleum-derived fuel into synthetic fuel in amounts that maintain a minimum threshold of aromatics can alleviate seal swell problems. It is imperative that the solution to the seal swell problem not negate the other advantages of using an F-T fuel. Addition of aromatic species could increase the soot-forming tendencies of the fuel, and blending of petroleum-derived fuel in significant portions incrementally decreases the purity advantage. It would be advantageous to find a seal swell enhancing species or mixture that could be added to F-T fuels at low concentrations, and would not have a deleterious affect on the thermal stability.

This work describes an approach to alleviating seal swell concerns with an eye towards preserving the thermal stability of F-T liquids. Using previous results to identify trace polar species in petroleum fuels^{2, 3} as well as computational modeling of the interaction energies between individual chemical species and a monomer of nitrile rubber (NBR), a suite of compounds was chosen to spike into surrogate fuels and synthetic fuels to determine the degree to which they swelled NBR o-rings. Subsequent to finding a promising swelling agent, the thermal stability of the spiked surrogate was compared to that of the original pure surrogate to determine any deleterious affects.

Experimental

Materials and Samples. Nitrile rubber o-rings were chosen as the test material, as it is a widely used material in fuel applications. Buna-N (nitrile) o-rings with o.d. of 1.9 mm and thickness of 0.3 mm were purchased from Parker Seals, Inc., and were used as obtained. Individual chemical species used for spiked swelling tests were purchased from Sigma-Aldrich and were used as obtained. Fuels used for swelling tests included petroleum-derived fuels (Jet-A and JP-5), n-dodecane (surrogate for synthetic jet fuel), and synthetic jet fuels (S-5 and S-8).

Swelling Tests. All swelling tests were performed according to ASTM Methods D-1414 and D-471.

Thermal Stability Tests. A reaction tube consisting of a 20-cm section of stainless steel tubing fitted with Swagelok™ fittings was used to perform high-temperature stressing of the fuels being studied. A fuel volume of 10 mL was placed inside the reactor, and the headspace was pressurized to approximately 6.8 atm with air. The sealed reactor was then placed in a sand bath, where the temperature was raised for a given period of time, and then the reactor was removed and the temperature rapidly decreased by immersion in cold water. The reactor was opened and the liquid sample was filtered to collect any solid deposits suspended in the liquid. The mass of solids was determined, and the filtered liquid was characterized using GC-MS.

Gas Chromatography Mass Spectrometric Analysis. Samples were analyzed using both polar and nonpolar columns installed in GC-MS systems. One instrument was an Agilent 6890 GC – Agilent 5973 MS equipped with a Stabilwax-DA column (60 m x 0.25 mm ID, 0.5 μm df, Restek, Bellefonte, PA). The other instrument was an Agilent 5890 GC – Agilent 5970 MS equipped with a Petrocol 50.2 column (100 m x 0.25 mm ID, 0.25 μm df, Supelco, Bellefonte, PA). Samples were injected either manually (5890-5970 system) or using an Agilent automated liquid sampler (ALS 7683 on the 6890-5973 system). Data processing was done using

ChemStation GC-MS software (Agilent), and peak identifications were accomplished by library matching using ChemStation (Agilent) and AMDIS 32 (NIST). Chromatographic separation was done using the oven program shown in Table 1.

Table 1. Chromatographic separation parameters used for liquid fuels separations.

Inlet	Temperature: 280 °C Split ratio: 1:50 Injection volume: 0.5 µL Constant flow @ 1.0 mL/min
Oven	35 °C for 5 minutes 3 °C/min to 280 °C
Columns	Stabilwax-DA (Restek) 60 m x 0.25 mm id Petrocol-50.2 (Supelco) 100 m x 0.25 mm id

Computational prediction of interaction energies. Computational modeling of the interactions between specific organic molecules and the isobutyronitrile functionality was carried out using a scheme adapted and extended from previous work conducted at the National Energy Technology Laboratory (NETL)^{4,5}. Implementation of this scheme consisted of performing ab initio calculations using the Gaussian 03 package⁶ to determine optimized structures at the second order Møller-Plesset (MP2) level of theory using the cc-pVDZ basis set for organic molecules and the isobutyronitrile monomer as the model polymer. Fully optimized combined structures for each of these molecules with the isobutyronitrile monomer were calculated with the same cc-pVDZ basis set and at the MP2 level of theory. Finally, single point energy counterpoise calculations were made to determine the Basis Set Superposition Error (BSSE) corrected interaction energies for these molecules with the model polymer.

Results and Discussion

Because the paraffinic portion of a petroleum-derived fuel makes up a significant portion of the matrix but does not swell seals, it can be surmised that potentially active species are the aromatics and/or the trace polar (heteratomic) species, both of which are present at much lower levels. Previous work showed that much of the polar material in a petroleum fuel is comprised of aromatic nitrogen species, such as alkylbenzenamines, and aromatic oxygenates, such as phenols^{2,3}. Computational efforts also predicted that the highest degree of interaction between a potential swelling agent and a monomer of NBR, leading to seal swell, would be provided by species having aromatic character along with a polar constituent⁵. Therefore, based on both the compositional analysis and the computational modeling, a suite of species with these characteristics were identified as potential seal swelling additives. The compounds were individually spiked into the synthetic fuel at 1% (vol) and the swelling was measured⁵. The data for these studies is shown in Table 2.

The experimental data verifies that which was predicted by the computational modeling. This can be seen by comparing the predicted interaction energy and observed swelling for fully saturated decalin, aromatic naphthalene, and aromatic and polar 1-naphthol. Species having an aromatic ring as well as a polar group attached to the ring do show a propensity to swell the NBR o-ring. Other species having similar structures were tested, including phenol, benzyl alcohol, and tetrahydronaphthol.

Table 2. Free swell of NBR o-rings for selected species.

Test species	Interaction Energy (kcal/mol)	Volume swell (%)
S-5 + decalin (1%)	-1.9	0.8 ± 0.1
S-5 + naphthalene (1%)	-1.4	1.2 ± 0.5
S-5 + 1-naphthol (1%)	-6.6	13.3 ± 0.6
S-5 + phenol (1%)	-6.2	15.4 ± 1.0
S-5 + benzyl alcohol (1%)	-7.1	17.5 ± 0.4
S-5 + 5,6,7,8-tetrahydro-1-naphthol (1%)	-6.2	7.3 ± 0.4

Upon finding a promising suite of species that could induce significant seal swell, these potential additives were tested for their affect on the thermal stability of a surrogate F-T fuel (n-dodecane). Fuels were spiked with each species and were subjected to thermal stressing at 350 °C for durations of both 6 and 12 hours. After stressing, the reactor was quickly cooled and the liquid material was filtered. The mass of deposits on the filter paper after the 12-hour tests is shown in Table 3. For the 6-hour tests, deposit masses were too near the detection limit of the balance; however, visual inspection of the filter papers indicated that both of the petroleum fuels (Jet-A and JP-5) created dark yellow-brown deposits while the dodecane and additized dodecane left only trace amounts of filterable material. For the 12-hour tests, where oxygen levels were replenished periodically, the trend was similar. Each of the petroleum fuels demonstrated greater deposition than both the synthetic fuel and the synthetic fuel additized with benzyl alcohol.

Table 3. Mass of deposits found after filtering of thermally stressed liquid fuels and mixtures.

Mixture	Mass of deposit (g) 12-hour test
Jet-A	.0040
JP-5	.0026
S-5	.0016
S-5 + 0.5% benzyl alcohol	.0006

Compositional Analysis of Stressed Liquids. Using GC-MS, each of the filtered liquids from the thermal stress test was characterized. This was done to explore whether the presence of the additive affected the product suite generated from the elevated-temperature reactions. Figure 1 shows the chromatograms for samples of neat dodecane and dodecane with 1% benzyl alcohol after both had been thermally stressed for 6 hours. The chromatogram for the neat dodecane shows the generation of n-alkanes and 1-alkenes of carbon number C5 through C10. (In the figure, peaks for the 1-alkene species are noted with “=” while the peaks for the normal alkanes are noted with “n”.) The chromatogram also shows the generation of alkanes (normal and branched) of carbon number C14 through C24. Previous work using tetradecane has demonstrated the formation of a similar product suite at high temperature ⁷. The primary oxygen-containing species that were formed include dodecanols and dodecanones, along with

some tetrahydrofurans and tetrahydropyrans. When benzyl alcohol was added, there was very little difference in the types and amounts of oxygen-containing species formed. The primary difference was that much less of the C5 through C10 n-alkanes and 1-alkenes, as well as the C14 through C24 normal and branched alkanes, were formed. Because these species are likely formed through free radical processes, and because benzyl alcohol is a noted free radical scavenger, the presence of benzyl alcohol reduces their production⁸. Moreover, the production of oxygen-containing species was similar for both mixtures. Therefore, it does not appear that the presence of this swelling additive had a detrimental effect on the stability of the liquid.

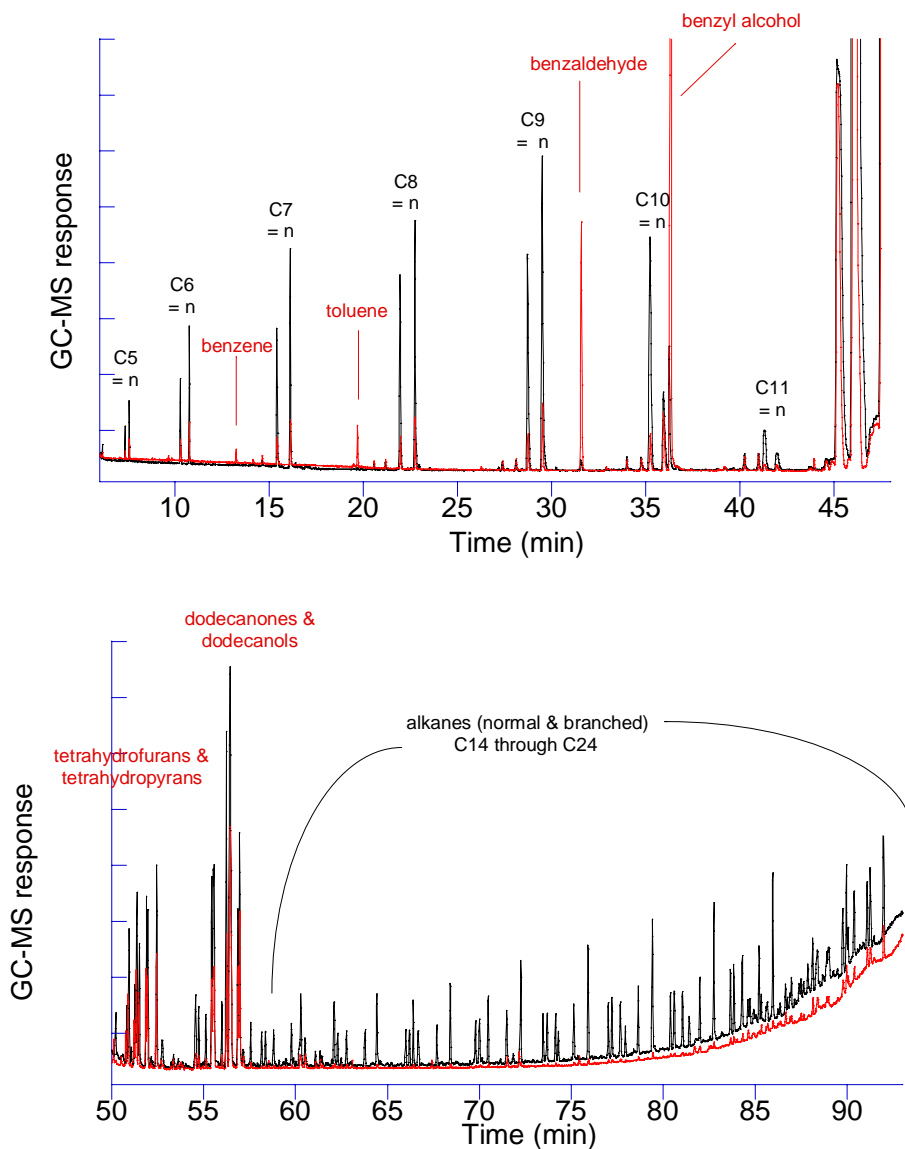


Figure 1. GC-MS chromatograms of thermally stressed n-dodecane (black) and thermally stressed n-dodecane + 1% benzyl alcohol (red). The top overlay shows initial ~45 minutes of the chromatograms, while the bottom overlay shows the final ~45 minutes.

Conclusions

This work has shown that the addition of benzyl alcohol to a synthetic surrogate imparts a similar degree of swelling compared to a petroleum-derived jet fuel. This agrees with results from computational modeling of the interaction between an individual species and a monomer of nitrile rubber. Further, the addition of benzyl alcohol does not appear to degrade the thermal stability properties of the synthetic surrogate, as the quantity of deposits generated from thermal stressing of a synthetic fuel (S-5) was similar to that seen when benzyl alcohol was added to the S-5 at 0.5% (vol). This work indicates that it may be possible to impart interchangeability to a synthetic fuel by the addition of low concentrations of benzyl alcohol. However, additional work on the additized fuel (or surrogate) is required to ensure that other properties of the fuel are not negatively affected.

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