Napalm as an energy resource: a study of the molecular weight distribution of polystyrene in napalm and its use in middle distillate fuels

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Abstract

The large quantity of napalm that is currently being treated as hazardous waste represents a viable energy resource that is too valuable to waste. However, there are significant problems to be overcome before this material can be used as an energy source. The scientific and environmental problems include: the broad molecular weight distribution of polystyrene, solubility and compatibility in a fuel matrix, methods to ensure complete combustion, high benzene concentration, low flash point due to the presence of gasoline, and safety in transportation and handling. In this paper, we present data on the molecular weight distribution of the polystyrene present in the napalm mixture, extraction of the gasoline and benzene from napalm, solubility of napalm in middle distillate fuels, simulated burner characteristics of napalm fuel mixtures, and accelerated storage stability studies of napalm fuel mixtures. Published by Elsevier Science B.V.

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1. Introduction

There are more than 3.4 million gallons of napalm in various military storage facilities in the USA. The fate of this napalm is currently in question. Suggestions have ranged from disposal as hazardous waste, to chemical separation into its components, to

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incineration, to industrial use. The chemical composition of napalm is by weight, 20% benzene, 43% polystyrene and 37% gasoline [1]. The high concentration of benzene and the low flash point of the gasoline in the napalm present environmental problems with any direct energy use of this mixture. The molecular weight of the polystyrene in napalm ranges from a low of several hundred to a high of more than 1 000 000 MW. The destruction of this material by incineration is complicated by both legal and political considerations. However, our research shows that if this material were blended in low concentrations with commercial fuels, it could provide a significant source of energy.

Middle distillate fuels and fuel oils that are used for industrial heating or electric power generation represent credible candidates for the use of this energy source. As shown in Table 1, the flash point and the boiling point of the fuels are the two criteria that napalm would impact the most [2–4]. These industrial consumers have the advantage of bulk storage, little direct fuel contact with people, and a safety network of fuel handling professionals. Due to the high concentration of polystyrene, napalm itself could not be burned directly as a fuel because the spray nozzles of practically all burners in combustors would plug. In addition, the flash point of napalm is very low and this presents a significant safety hazard for both storage and use. A further consideration is that fuel compatibility problems of napalm are significant. In order to overcome this problem, a high aromatic middle distillate fuel along with a co-solvent must be used as the diluent.

Automotive and other transportation fuels, gasoline and diesel, present too many handling, logistic and consumer safety problems for napalm to be used as a diluent in these fuels. Since many vehicles are out of tune, the use of these fuels for transportation purposes would result in significant unburned hydrocarbon emissions to the atmosphere, including benzene.

Heavier oils, such as Number 5 or Number 6 fuel oils, usually require preheating before burning. If napalm were directly added to these fuels, the benzene and gasoline, because of flash point considerations, would impose both handling and fire hazards.

In this article, we present our data on napalm constituent extraction and solubility in various low molecular weight solvents, types of middle distillate and heavier fuels, and

Table 1
General ASTM specifications for the various types of fuels

Specification	Jet fuel JP-8	No. 2-D[a]	No. 1[b]	No. 2[c]	No. 4[d], heavy	No. 5[e], heavy
°API gravity	37	40.1	35	30	–	–
Total sulfur percentage	0.3	0.5	0.5	0.5	–	–
Boiling point°C	300	338	288	338	–	–
Flash point°C	38	52	38	38	55	55
Pour point°C	–	−6	−18	−6	−6	–
Ash percentage mass	–	–	–	–	0.10	0.15

[a]Low speed, high load engines.
[b]Special purpose burners.
[c]General purpose heating fuel oil.
[d]Commercial/industrial burners.
[e]Industrial burners, preheated fuel.

in fuels with co-solvents. Also presented are the results of accelerated storage stability studies and burner characteristics of these mixtures. These studies are predictors of ambient tank storage stability.

2. Materials and methods

2.1. Fuels

Several fuels were used as diluents. They included: marine gas oil (MGO); a low aromatic middle distillate (20 wt.% total aromatics, identified as 97-36); a high aromatic middle distillate (44 wt.% total aromatics, identified as 97-44); a JP-5 jet fuel; and a JP-8 jet fuel. Commercial Jet-A is very similar to the military jet fuel, JP-8.

2.2. Solvents

Other solvents used were acetone, acetaldehyde, benzene, ethyl acetate, toluene and xylene(s). They were all obtained from Fisher Scientific and used as received. Absolute ethyl alcohol was obtained from US Industrial Chemicals and used as received. Polystyrene, in various molecular weight ranges, was obtained from Polysciences and used as received.

2.3. Napalm synthesis

Napalm was prepared by dissolving 43 g of polystyrene in 20 g of benzene. The polystyrene ranged in molecular weight from 800 to 1 000 000 MW. The percent composition and the ranges of molecular weights were 90% 800–5000 MW, 8% 50 000 MW, and 2% 1 000 000 MW. This duplicates the MIL Spec. for commercial napalm [1]. After complete solution of the polystyrene, 37 g of unleaded gasoline were added to the solution under constant stirring by a Teflon stir bar. The resultant napalm was kept in a Teflon stoppered flask in a hood at room temperature and isolated from all ignition sources.

2.4. Napalm solution preparation

The napalm mixtures were prepared by weight because of the high viscosity of the napalm. The solutions prepared were 5%, 10% and 20% napalm by weight. The solvents used for dilution were acetaldehyde, acetone, ethyl acetate, ethyl alcohol, toluene, xylene, MGO, gasoline, both high and low aromatic middle distillate fuels, and both JP-5 and JP-8 jet fuels. In addition, co-solvents of 2:1 fuel to toluene/xylene, 3:1 fuel to toluene/xylene, and 4:1 fuel to toluene were employed. The resultant solutions were all stirred (Teflon stirring bar) at room temperature for 1 h in a hood with an aluminum foil cover before a solubility determination was made. The solutions were then stored in brown borosilicate bottles with Teflon lined caps for further testing. A quantitative soxlet extraction procedure using a Kontes Glass 585250 apparatus was performed for several of the mixtures to demonstrate separation from the polystyrene.

2.5. Instrumental method

The samples were analyzed by a Hewlett Packard (HP) Model 6890 gc and data system. An all-glass gc inlet system was used in conjunction with a 0.32 mm × 30 m fused silica capillary column, HP cross-linked 5% phenyl methyl silicone. The injector temperature was 250°C and the detector was 320°C. The column flow was 1 ml/min. The temperature program started with an initial temperature of 60°C for 5 min, a ramp of 5°C/min, to a final temperature of 260°C. The chromatograms were recorded and integrated on a HP data system.

2.6. Simulated burner

A simulated burner was constructed to test nozzle plugging and soot formation. The brass burner consisted of an 1/8 in. i.d. nozzle orifice surrounded by a 1/2 in. air mixing chamber. The outer chamber was drilled and tapped for a 1/8 in. air line. The fuel was pumped through a 1/4 in. tube to the nozzle orifice by a syringe pump with a 30 ml capacity syringe. The air to the mixing chamber was operated at 5 psig or less. The burning of the napalm fuel mixtures were for a period of 15 min at which time the burn was suspended and the nozzle examined for clogging. A second method for measuring burner clogging consisted of an oxygen source added internally to the fuel in the form of hexanol (40% hexanol, 60% fuel by volume). A qualitative procedure for measuring soot was also used. It consisted of an inverted 10.5 cm Buchner funnel connected to a vacuum system. After the vacuum was started, a filter was placed in the funnel. The burner was suspended 30 cm below the funnel and ignited. The filter collected the soot that was formed. The filter was then weighed to give a measure of the soot yield.

2.7. Storage stability tests

The napalm fuel mixtures were tested for fuel instability and incompatibility using a modified ASTM method D5304-94 [5]. In brief, this method is described as: 100 ml samples contained in 125 ml borosilicate glass brown bottles were subjected to a 1 week, 80°C time–temperature regimen at 50 psig overpressure of air. After the stress period, the samples were cooled to room temperature. These samples were tested for sediment by a gravimetric technique and for peroxidation by a modified procedure based on ASTM D 3703-92 [6].

3. Results and discussion

The huge amount of surplus napalm possessed by the US military is too large to simply ignore or destroy by purely destructive methods such as incineration. The energy equivalent in this fuel source could represent a significant saving to both electrical power generation plants and municipal heating plants. The energy content of the surplus napalm was reported to be 18,383 Btu/pound [1].

Table 2
Solubility of napalm as a function of the molecular weight of polystyrene in pure solvents and fuels

Solvent	Polystyrene molecular weight and napalm solubility		
	800–5000	50 000	> 1 000 000
acetone	soluble	soluble	soluble
acetaldehyde	soluble	soluble	soluble
ethyl acetate	soluble	soluble	soluble
ethyl alcohol	insoluble	insoluble	insoluble[a]
toluene	soluble	soluble	soluble
xylene(s)[b]	soluble	soluble	soluble
diesel fuel (high aromatic)	soluble	soluble	insoluble
diesel fuel (low aromatic)	soluble	soluble	insoluble
jet fuel, JP-5	soluble	soluble	insoluble
jet fuel, JP-8	soluble	soluble	insoluble
MGO	soluble	insoluble	insoluble

[a] By GC.
[b] A mixture of *ortho*, *meta* and *para* isomers.

This material, because of its benzene and gasoline content, is not suitable for direct use as a fuel and must be mixed as an additive to some other fuel matrix. Table 2 illustrates the solubility of napalm in various organic solvents. Low molecular weight non-aromatic and aromatic solvents containing aldehyde or ketone functional groups, i.e., acetone and acetaldehyde, give solutions that are miscible in all proportions. However, these cause a significant lowering of the flash point of any fuel to which this mixture would be added.

The alcoholic –OH group negated the solubility of polystyrene, but the ethyl alcohol did extract the benzene and gasoline, as demonstrated from the gc results, Fig. 1. A
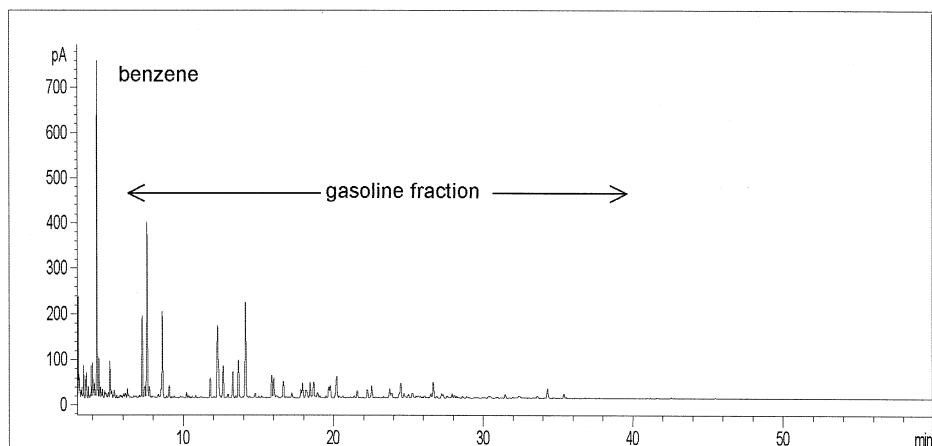

Fig. 1. The ethyl alcohol fraction from a Soxhlet extraction of napalm showing that benzene and gasoline are separated from the polystyrene. The large peak corresponds to benzene and the other peaks correlate with the gasoline that was used to synthesize the napalm sample.

quantitative extraction was performed with ethyl alcohol in a soxlet extraction procedure. As shown in Fig. 1, the benzene and the gasoline components were extracted by the ethyl alcohol. The largest peak in the chromatogram is that of benzene and the others are all from the gasoline components. For clarity, the ethyl alcohol solvent peak is not shown on the chromatogram and the benzene peak was scaled as the largest peak. The polystyrene remained as a solid in the extraction thimble. The extraction efficiency was greater than 99%, based on the recovery of gasoline and benzene.

Low molecular weight esters are excellent solvents for napalm. Ethyl acetate and napalm were miscible in all proportions. Alkyl and aromatic esters have the advantage of a higher flash point than the corresponding ketones or alcohols, but have the disadvantage of increased thermal stability. Napalm was not directly soluble in middle distillate fuels (diesel and jet). The total aromatic content of the fuel did not make a significant difference in the direct solubility of napalm. However, in these distillate fuels, the gasoline and benzene were extracted from the napalm, leaving the polystyrene to coat the container surfaces. This observation was confirmed by noting the presence of gasoline and benzene peaks in the gas chromatograms of these fuel mixtures.

MGOs behaved quite differently. The MGO was absorbed by the polystyrene causing a ten fold increase in the solid phase. This was the most unwanted of all fuel matrix scenarios.

The solubility information from pure solvents illustrated that co-solvents might be successfully employed to enhance the overall solubility of napalm. For this work, no low molecular weight ketones, aldehydes, or alcohols were used as co-solvents for flash point and safety in handling reasons. The flash point of the final mixture was one of the most important considerations. The flash point of toluene is 4.4°C, xylene is 27°C to 32°C depending on the isomer, ethyl acetate is −4.4°C, and for acetone it is −18°C [7], while the flash point for napalm is −26°C [1]. Thus, the choice for a co-solvent based on this most important standard was toluene or xylenes. They were used as co-solvents with middle distillate (both low aromatic content, and high aromatic content) fuels, jet fuels and MGOs. The low aromatic middle distillate fuel sample (designated 97-36) contained a total of 20% aromatics, while the high aromatic fuel (designated 97-44) contained 44% total aromatics. Solutions were made up that consisted of fuel to toluene or xylene mixtures from a high of 2:1, fuel:toluene (xylenes) to a low of 4:1 fuel:toluene (xylenes) and in one case a 1:1 fuel to toluene ratio. Table 3 summarizes the results from these runs. In Table 3, the results for the co-solvents toluene and xylene are given, since these were the solutions tested for accelerated storage stability and burning characteristics. It is to be noted than none of the fuels completely dissolved the napalm. If lower flash point co-solvents were used as diluents, this would present considerable problems in fuel handling, fuel storage, and most of all in future use of this mixture. All of the solutions were prepared under ambient conditions, as this would most likely be the conditions of commercial use and storage. With the high aromatic content (44 wt.%) middle distillate, the 2:1 and 3:1 matrix ratios (97-44 to toluene) represented the best solubility cases. When a 4:1 fuel to toluene matrix was employed, the napalm proved to be insoluble. With the heavier MGO fuels at a ratio of 2:1 MGO to toluene the solution displayed only a very slight turbidity. The turbidity reported in Table 3, in all cases, was due to the insolubility of the polystyrene in the fuel. At a higher concentration of 1:1

Table 3
Solubility of napalm with polystyrene of molecular weight greater than 1 000 000 in co-solvents

Co-solvents	Napalm solubility (20:1 co-solvent:napalm)[a]
Middle distillate diesel	
2:1 97-44:toluene/xylene	completely soluble
2:1 97-36:toluene/xylene	slightly soluble with significant turbidity
3:1 97-44:toluene/xylene	completely soluble
3:1 97-36:toluene/xylene	insoluble
4:1 97-44:toluene/xylene	insoluble
4:1 97-36:toluene/xylene	insoluble
Heavier oils	
1:1 MGO:toluene/xylene	completely soluble
2:1 MGO:toluene/xylene	soluble with slight turbidity
3:1 MGO:toluene/xylene	insoluble

[a]All concentrations by weight.

MGO to toluene the napalm was completely soluble, however, this was not considered a viable matrix for commercial use. The MGO was the only fuel that was tried at this higher toluene concentration.

Table 4 shows the accelerated storage stability results for the high aromatic middle distillate fuel 97-44 and fuel xylene mixture, both a 2:1 and a 3:1 fuel to toluene (xylene) ratio. The stress time/temperature matrix of 1 week at 80°C and 50 psig of air was selected based on its severity of conditions. This tests mimics the ambient behavior for approximately one year of tank storage. To pass this test, a fuel must produce less than 1.5 mg of solids from 100 ml of fuel. A fuel that successfully passes this test is considered to be storage stable. The marginally stable fuel (97-44) was selected to see whether the napalm would induce further instability and/or precipitate the polystyrene from the napalm. The total amount of sediment is shown in Table 4. The results showed that the fuel:toluene solutions are unstable under accelerated storage conditions. A microscopic examination of the deposit from the fuel:toluene matrix revealed that the sediment was composed of finely divided polystyrene and not some product derived from a chemical reaction with other compounds in the fuel itself. It was thought that the accelerated storage test results might be influenced by the benzene and gasoline

Table 4
Accelerated storage stability results for fuel 97-44 and napalm doped 97-44 xylene mixtures at 1 week at 80°C and 50 psig air + 50 psig N_2 total pressure

Sample fuel napalm mixture	Sediment produced from napalm (mg/100 ml fuel) at various molecular weight of polystyrene			
	800–5000	50 000	> 1 000 000	Peroxide number
Fuel 97-44 neat	3.4	3.4	3.4	0
97-44 napalm doped 3:1 fuel:solvent matrix	0	0	1.7	0

evaporating from the samples. As the benzene and gasoline concentrations decrease, so does the solubility of the polystyrene. To test this hypothesis, a second time/pressure accelerated storage test was performed. In this test, the pressure was raised to 100 psig by adding an additional 50 psig of nitrogen and the co-solvent was changed to xylene for flash point considerations. This higher pressure was required to keep the lower molecular weight gasoline fraction in solution. We have employed this increased pressure technique successfully in other instances when the fuel to be tested contained low molecular weight components. The results from this second test showed that the napalm, dissolved in a 2:1 ratio of fuel to solvent, easily passes the accelerated storage stability test and should prove to be storage stable for at least a year. In addition, the storage stability test for the 3:1 fuel to solvent mixture illustrated that this solution was also stable. In this second procedure, the fuel napalm mixtures actually produced less sediment than the fuel itself. The values for the napalm:fuel mixtures are low because the increased pressure was responsible for keeping the low molecular components (including the co-solvent) in solution and thus the polystyrene in solution. No evidence of polystyrene coating the surface of the glass bottles was observed. To further demonstrate that the polystyrene was still in solution, after the stressed fuel samples were filtered and the sediment weighed, hexane was added to the solution and the polystyrene immediately started to precipitate.

The peroxide number (mg peroxide/kg fuel) for the fuel and the fuel to toluene napalm mixtures are given in Table 4. The results show that no peroxide was formed in the fuel or in any of the two fuel to toluene napalm solutions. The lack of formation of peroxide species is important in that it showed that the addition of the napalm did not catalyze reactions that produced these active oxygen species. Peroxide species are the most active oxygen compounds present in any fuel. Peroxidation can be strongly implicated in any subsequent fuel degradation [8,9].

Two types of burner simulations were conducted to measure plugging from the presence of the polystyrene and to check on the sooting of the fuel and the napalm fuel mixtures. The fuel, in one case, was diluted by volume 40%:60% with hexanol to internally add more oxygen to the fuel. The fuel and fuel napalm mixtures burned in a similar fashion. In the second case, the fuel nozzle was surrounded by air under pressure. This burner arrangement proved to be the best because of the large volume of air that could be used by the flame. The flame burned cleanly and produced no significant quantities of soot. More importantly, the burner nozzle showed no signs of plugging from the presence of the higher molecular weight (50 000–1 000 000 MW) polystyrene.

4. Conclusion

Napalm can be safely handled and used as an energy source if it is used in the presence of co-solvents. The presence of low flash point components (gasoline and benzene) and the high molecular weight polymer polystyrene complicates commercial use of napalm. By the use of aromatic co-solvents, i.e. toluene or xylenes, which have higher flash points than low molecular weight solvents, napalm can be safely handled

and dissolved in middle distillate fuels at a ratio of 2:1 or 3:1 (fuel:co-solvent). The accelerated storage stability test showed that these fuel mixtures would be storage stable for time periods of at least one year. These fuel mixtures burn cleanly and did not plug the nozzle of the burner. This solution could provide a viable energy resource that can be used in commercial applications such as electrical power generation, central heating plants, or industrial processes that require heat.

Acknowledgements

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