

A study on doping of high energy boron powder into liquid fuel JP-10

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The immobilization of high energy material particles into liquid fuels to enhance its energy content for the volume limited aerospace application is an excellent idea as these particles possess higher heating values than liquid fuels. Among different type of metals and metalloids, elemental boron has highest volumetric heat of combustion (136 kJ/cm³). Technological issue of using boron in liquid fuel is that boron particles undergo aggregation and coagulation which results in precipitation of large size particles. This work is undertaken to explore the possibility of introducing boron into liquid fuel JP-10. This liquid fuel (exo-THDCPD) is prepared in house via single step method by using mesoporous zeolite supported metal nano-catalyst in a high-pressure reactor. The boron particles of 640 nm average particle size has been obtained from one of our sister lab and characterized. Selection of surfactants has been done for better dispersion of boron particles into liquid fuel. A variety of surfactants, such as oleic acid, sorbitan-oleate, and tween, have been tested for stability of boron particle suspensions and evaluated by sedimentation test i.e. visual method and by zeta potential meter. Different concentrations of boron particles like 0.5, 1, 2 and 10 wt % of boron into JP-10 fuel is dispersed by using surfactant and the mixture is subjected to probe sonicator for 30 min under ambient temperature of 25–30°C as good mixing must be ensured in order to disengage the particles. Sample of 10 wt% boron into liquid fuel JP-10 with 0.5 and 1.0 wt% surfactant addition (combination of Tween80 and Span80) has given stable suspension for 144 and 192 h, respectively.

Keywords: Boron doping, Dispersion, High energy material, Liquid fuel JP-10, Surfactant, Zeolite supported metal nano-catalyst

Introduction

The development of high-speed aerospace vehicles and their volume limited propulsion system always constructs the demand of cost-competitive high energy density fuel which can liable to improve the volumetric energy density as well as ignition and combustion characteristics¹. Up to now, Fuels derived from polycyclic hydrocarbons have made impressive advancements in synthesis (e.g., RJ-4, RJ-5, RJ-7, JP-5, JP-8 and JP-10). In comparison to conventional fuels, JP-10 (exo-tetrahydrodicyclo-pentadiene) is one of the most promising fuels, with a volumetric energy of 39.6 MJ/L and a very cold freezing point (-79°C)². In spite of this, it is desirable to boost the volumetric energy content of liquid fuels. A number of researchers have investigated the effects of doping very high energy metal or metalloid particles with liquid fuels (micron particles and nanoparticles) over the past few decades^{3,4}. Among different type of metal particles, boron (Fig. 1) is most attractive with both

volumetric (136 kJ/cm³) and energy densities of approximately 40% higher than hydrocarbon fuels based on gravimetric analysis (58.5 MJ/kg)^{2,5,6}.

Boron demonstrates its performance as potential energetic particle but to get stable dispersion of boron particle into liquid fuel (i.e., solid-liquid suspension) is still a key challenge because of higher density of solid boron particle than that of synthesized JP-10 fuel and inherent property of boron particle to coagulate and aggregate due to strong van der Waal's force which results large agglomerate particles. Previous studies show that by modifying the surface of boron using ionic, non-ionic or amphoteric compounds which have hydrophilic polar head and a long hydrocarbon chain with a hydrophobic tail, researchers were capable to get the stable suspension of metal particles in liquid fuel⁷. Oleylamine protected Pt and Pd particles dispersed in JP-10 were synthesized that can promote the endothermic cracking reaction in past research⁸. The addition of

surfactant containing boron particles with liquid fuel is shown in Fig. 2. In this communication, we demonstrate the surfactant protected metal boron particle that can be highly dispersible with high concentration in polycyclic liquid hydrocarbon JP-10 fuel and improve the energy content of the conventional hydrocarbon fuel.

Experimental Section

Materials

The boron particles of 640 nm average particle size were of research grade and obtained from our sister lab's pilot plant at Pune. Liquid fuel JP-10 was prepared in house by a new kind of solid catalyst which is Ni supported over MCM-41. The structural analysis of JP-10 fuel was carried out by FTIR, H^1 and C^{13} NMR technique and fuel meets with the specifications of MIL-DTL-87107D standard⁹. Oleic acid, Tween-80, Span-80 etc. were used as dispersion stabilizer to prevent the aggregation of particles and all were purchased from Sigma-Aldrich with 99% purity.

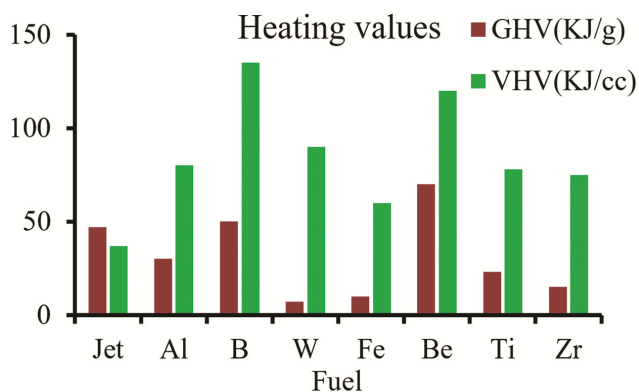


Fig. 1 — Graph for gravimetric (GHV) and volumetric (VHV) heating values of few high energy metal particles

Selection of surfactant for the stable suspension

To achieve long-term stable suspensions of metal boron particles in liquid fuel and address the issue of poor colloidal stability, Bancroft's theory and hydrophilic-lipophilic balance (HLB) have been combined and tested. Metallic boron particles make up the dispersed phase of the system to be stabilized, whereas jet fuel constitutes the continuous phase. Using Bancroft's suspension theory, one can determine the type of surfactants (or dispersants and emulsifiers) needed for settling experiments.

Many available surfactants offer benefits such as enhanced stability, formulation flexibility and broader compatibility when used as dispersants. Oleic acid, Spans and Tweens are classified as non-ionic surfactants; additionally, since these two dispersants and wetting agents are effective together, they produce a wide range of HLB values. The initial selection of oleic acid and Span-20 (S-20) and Span-80 (S-80) was based on their lipophilic nature and low HLB ratings^{10,11}. The weighted average HLB value of surfactant was used to find the mixture HLB value. It was tested separately and in combination with Tween-20 with an HLB value of 16.7, and Tween-80 with an HLB value of 15.

Dispersion of boron in liquid fuel

A stable suspension was made by adding surfactant to the hydrocarbon fuel and mix thoroughly to ensure complete miscibility. The hydrocarbon-surfactant solution was mixed with micro-boron particles, then de-aggregated with a probe-type sonicator. The monolithic micron boron particles degrade by the influence of ultrasonic waves and dispersion increases. Sonication was typically performed for 30 min, with the suspension temperature maintained near the 25–30°C.

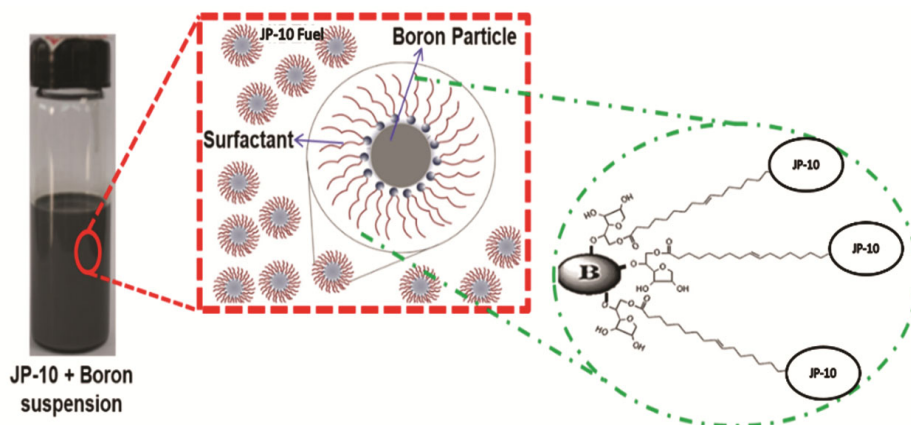


Fig. 2 — Diagrammatic representation of addition of surfactant with JP-10 and boron particles

Sonication of the suspension was followed by regular snapshots of the glass vessel containing it. Sedimentation zone height was measured and monitored to evaluate stability. The fuel was prepared by dispersing 0.5, 1, 2 and 10 wt % of boron particles in liquid fuel JP-10 containing 0.5 and 1 wt.% of surfactant. A standard recipe includes 89.28% of JP-10 fuel, 8.92% of boron particles, and 1.78% of surfactant for total weight of 16.8 g mixture.

Characterization

The synthesis of JP-10 fuel was done in-house by single step method in which a new kind of solid Ni nanoparticle immobilized into support MCM-41 (purely siliceous) catalyst was used to investigate the catalytic activity for DCPD hydro-conversion to exo-THDCPD under suitable reaction conditions i.e., 140-150°C temperature and hydrogen pressure range 300-400 psi. The reactions are monitored by a capillary column (0.25 mm x 0.25 m x 30 m) using flame ionization detector (FID). The structural elucidation of the product was collected by proton nuclear magnetic resonance (^1H NMR) (JEOL), spectra were recorded in CDCl_3 at 500 MHz field strength. Chemical shift values are reported in ppm relative to tetra-methyl silane (0.0 ppm) as an internal reference. The physico-chemical properties such as density (Anton Parr DMATM 35), freezing point, and heat of combustion measured by bomb calorimeter

Model 6200 (Parr Inst. Company USA) have also been evaluated and compared with the MIL standard (MIL-DTL-87107D) specification.

High resolution field emission scanning electron microscopy (FESEM) instrument to observe the morphology of the boron particles and X-ray diffraction (XRD) was carried out by the Rigaku Ultima D-max 2500 V/PC X-ray diffractometer with $\text{Cu K}\alpha$ radiation source (40 kV, 200 mA). The metal contaminations could be tested by using Oxford INCA 250 energy dispersive X-ray microanalyzer. The long-term stability of boron particles in liquid fuel was characterized by the sedimentation test i.e., visual method and by M3-PALS 90° DLS Zeta Potential Analyzer.

Result and Discussion

Characterization of synthesized JP-10 fuel

The physico-chemical properties such as density, freezing point, viscosity, heat of combustion and flashpoint of synthesized liquid JP-10 fuel were measured by methods mentioned in the MIL standard and obtained results were compared with MIL-DTL-87107D specification as given in Table 1.

Characterization Boron particles

The FESEM characterization of amorphous boron powder is represented by Fig. 3 which revealed a large particle size range, with calculated average size of 640 nm. The FESEM images also indicate that the

Table 1 — Comparison of synthesized JP-10 fuel with specifications

Physico-chemical properties	Synthesized JP-10 fuel	MIL-DTL-87107D
Physical state	Colourless and odour like Naphtha	Colourless and odour like Naphtha
Net heat combustion (MJ/kg)	42.3	42.1
Viscosity (centistokes) at;		
-54°C	40	40
-18°C	11	10
Density @ 15°C/kg/L	0.935	0.935-0.943
Flashpoint (°C)	54	54
Freezing point (°C)	-79	-79

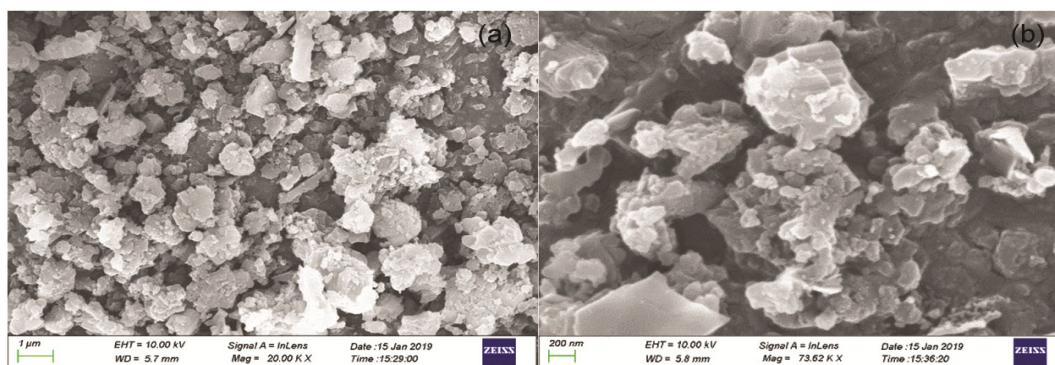


Fig. 3 — FESEM images of boron particles

micron-sized boron particles are agglomerated with no definite size and may form a metal oxide layer. The XRD data gives no significant peaks of rhombohedral, tetragonal crystalline boron phase which shows the amorphous nature of boron powder with minimal impurities such MgBx and BxO. A broad hump with minor corresponding impurities peaks were observed in XRD pattern which characterized the amorphous nature of boron (Fig. 4). XRD analysis of boron powder was performed using a Rigaku Ultima D-max 2500 V/PC X-ray diffractometer with a Cu K α radiation source (40 kV, 200 mA). The quantitative elemental measurement of boron was done by EDAX spectrometer indicating the minimum 5% impurities of Mg, O and other elements (Fig. 5 & Table 2). Thus, all the characterization indicating the amorphous nature of boron with 640 nm average particle diameter.

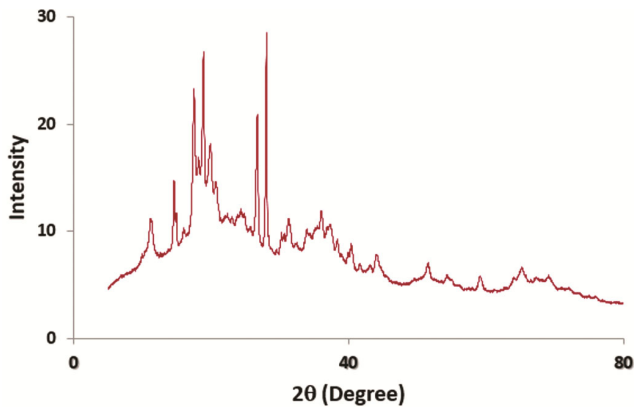


Fig. 4 — XRD pattern of boron powder used for experiments

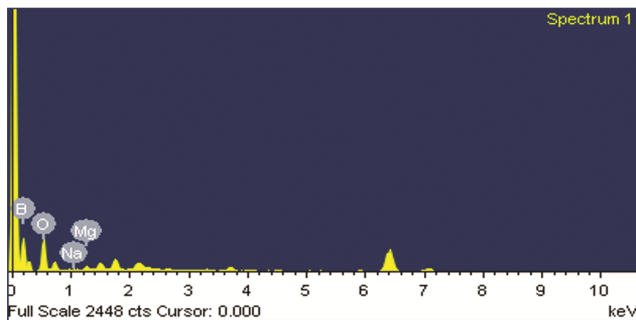


Fig. 5 — Graph of EDAX analysis

Table 2 — Quantitative elemental analyses of boron powder by EDAX

Element	Weight%	Atomic%
B K	77.90	84.01
O K	21.64	15.77
Na K	0.06	0.03
Mg K	0.39	0.19

Dispersion stability of the suspension

The general constituents of proposed high energy density fuel are the sub-micron to hundreds of micron size metal particles immobilized homogeneously in liquid fuel JP-10 (exo-THDCPD). The new fuel was prepared by dispersing 0.5, 1, 2 and 10 wt % of boron particles in liquid fuel JP-10 containing 0.5 and 1 wt% of surfactant. The long-term stability of boron particles in JP-10 fuel was characterized by the sedimentation test and zeta potential analyzer. Fig. 6(a) demonstrates the boron particle suspension in JP-10 fuel and about 75% of boron particle was agglomerated into larger particles result into sediment. Different types of surfactants were used as a dispersion stabilizer to prevent the aggregation of particles. Fig. 6(b) indicates the Span and Tween protected boron particles are well dispersed into liquid fuel with average particle size of 640 nm. The standard concentrations of Span and Tween were set at 0.5% and 1.0%. Any further increase in surfactant levels would result in a loss of stabilization. Furthermore, adding surfactants in amounts exceeding 1.5 wt% may lead to reduced energy release during combustion. The sonication of resultant mixture greatly improves the suspension of boron particles as

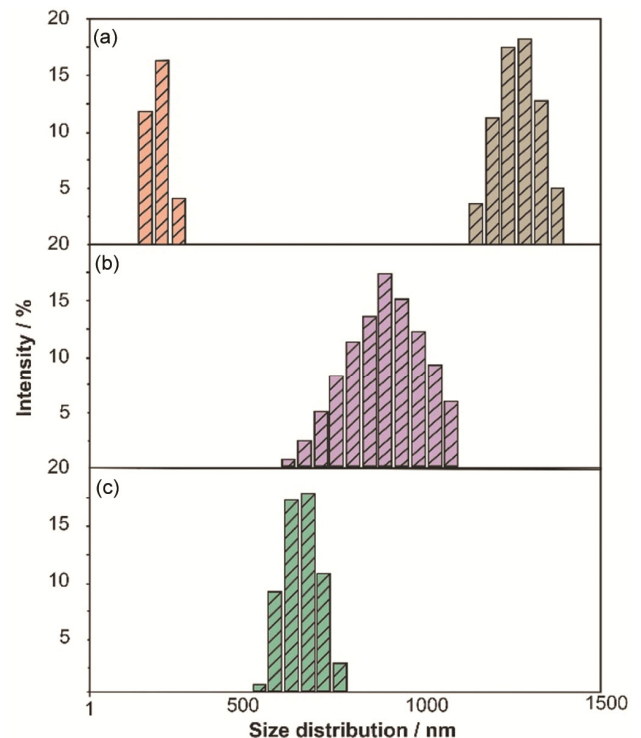


Fig. 6 — Particle distribution of (a) boron (1 wt. %) /JP-10 suspension (b) surfactant-protected Boron (1wt%)/JP-10 suspension, and (c) surfactant-protected boron (1 wt. %)/JP-10 suspension after sonication

Table 3 — Experimental results of boron suspension stability in JP-10 Fuel

Suspension	Sonication time (min)	Surfactant (wt%)	Stability time (h)			
			Oleic acid	Span80	Tween80	Span80 + Tween80
JP-10 + 0.5 wt% boron	30	0.5	53	230	120	281
	30	1.0	72	210	124	305
JP-10 + 1.0 wt% boron	30	0.5	59	195	126	226
	30	1.0	72	125	105	257
JP-10 + 10 wt% boron	30	0.5	48	120	120	144
	30	1.0	55	168	48	192

detailed in Fig, 6(c). The dispersion of surfactant protected boron particles was also investigated by the sedimentation test by visually and the suspension was allowed to standstill for different timings. The complete sedimentation of different used additives shown in Table 3. For a fuel sample of 10 wt% concentration of boron particles into liquid fuel, surfactant concentration of 0.5 wt% to 1.0 wt% were found best for the stable suspension.

Conclusion

The conclusions drawn from the above study are like, to achieve suspension stability of boron particles in liquid hydrocarbon fuel, surfactants or surface modification technology is much required. Surfactant effectively inhibits the particles agglomeration and boron particles are stable in liquid fuels. Among all the tested surfactants reported by various authors it is found that sorbitan-oleate is the best surfactants which is providing longer stability as a result of the increased number of active sites in its branched chain, creating bonds with the particle surface, thereby forming additional metal complexes. The results of overall dispersion in JP-10 fuel demonstrate that the 10 wt% concentration of micron boron containing 0.5 wt% to 1 wt% surfactant (combination of Span 80 + Tween 80) gives potential for stable suspension over 8 days. The view point of synthesizing boron suspended fuel summarized in present disclosure also assumes prominence for aerospace applications. Present study highlights the easiest methods for making suspension of boron particles into liquid fuel and gives general guidelines for preparation of stable suspension of boron in hydrocarbon liquid and the choice of surfactant. The most common drawback that needs to be taken seriously is the formation of an oxide layer on particle surface even at very low exposure of air. Hence, synthesis of controlled size boron nano-particle with surface modifications and passivation needed to be taken seriously. Introducing boron nanoparticles into liquid fuel can provide several benefits. Thus, we have found various strategies like surfactants or surface

functionalization of boron particles. Some capping methods reported are stable against oxidized boron particles, with few capping methods requires oxidation of boron particles, with high dispersibility and persistent suspension stability till several weeks.

Conflict of interest

The authors declare no conflict of interest.

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