

Boron : An Alternative Fuel

Kalpesh Mahajan
T.Y.C.E.



T. Vinod Sarma
T.Y.C.E.

Kalpesh Mahajan : I like reading and listening to music. I want to pursue higher studies in non-conventional energy sources.

T. Vinod Sarma : My hobbies include reading, computer gaming and sports. Along with academic activities I regularly take part in various sports events organized in the college. I want to pursue a career in Industrial Sciences.

Abstract

Present power crisis, the increasing environmental constraints and the depletion of fossil fuels at an alarming rate has given great momentum to the research in the field of alternative fuels. The following paper suggests one of the options in the race of sustainable energy sources – Boron. Boron is metalloid having atomic number 5. Boron was seen as a potential fuel in 1950's but the lack of any great breakthrough resulted in the diversion of the research funds to other options. The case for boron as fuel begins with a safety advantage. Although very combustible, it also is very hard to light. It has high energy density i.e. energy per unit pound and especially per unit gallon. Boron also has an advantage that in spite of energy being extracted from oxidation it does not produce any harmful gasses and combustion is purely emission free. Boron produces solid boria, which is solid below 200°C as a combustion product that can be recycled back to get the fuel. This would not only help in decreasing the environmental strain but will also lessen the worries of limited sources of fuel. The passivity of boron also gives rise to an advantage in storage of fuel. One of the problems in using boron as the fuel is need of high purity oxygen for combustion. The paper gives a brief account of working of boron economy – extraction of boron, its potential sources, boron combustion engine considerations, possible methods of recycling. The paper also reviews the work done in the development of boron as fuel, the direction and momentum of research.

1. Introduction

Alternative fuel, also known as non-conventional fuels, is any material or substance that can be used as a fuel, other than fossil fuels, or conventional fuels of petroleum (oil), coal, propane, and natural gas. The term "alternative fuels" usually refers to a source of energy which is renewable.

There are many disadvantages associated with the use of fossil fuels for running internal combustion engines, mainly economic. The price of oil is extremely volatile and the last 12 months have seen the cost per barrel rocket. In today's political climate the trend looks likely to continue upwards. Furthermore, burning gasoline releases carbon dioxide (CO₂), carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x), and hydrocarbons, amongst other gases, and particulate matter into the atmosphere, which cause serious environmental damage. But it is not just the environmental effects of harmful emissions – public health is also being compromised. For example, nitrogen oxides can react with volatile organic compounds in the atmosphere to form smog, which is known to increase respiratory problems in humans; and carbon dioxide is a "greenhouse gas" that contributes to global warming. Another concern is the problem of peak oil, which predicts a rising cost of oil-derived fuels caused by severe shortages of oil during an era of growing energy consumption. According to the 'peak oil' phenomenon, the demand for oil will exceed supply and this gap will continue to grow, which could cause a growing energy crisis by the year 2010 or 2020.

Now the need arises to have a sustainable alternative energy sources. Some of the alternatives available are:

- Solar energy
- Wind energy
- Energy from biomass

And perhaps boron.

2. Properties of Boron

Brown amorphous boron is a product of certain chemical reactions. It contains boron atoms randomly bonded to each other.

Optical characteristics of crystalline/metallic boron include the transmittance of infrared light. At standard temperatures, metallic boron is a poor electrical conductor, but is a good electrical conductor at high temperatures.

Chemically boron is electron-deficient, possessing a vacant p-orbital. It is an electrophile. Compounds of boron often behave as Lewis acids, readily bonding with electron-rich substances to compensate for boron's electron deficiency. The reactions of boron are dominated by such requirement for electrons. Also, boron is the least electronegative non-metal, meaning that it is usually oxidized (loses electrons) in reactions. Boron is also similar to carbon with its capability to form stable covalently bonded molecular networks.

3. History of Boron as a Fuel

In the early days of the Cold War Arms Race, aircraft and missiles

could not fly far enough or fast enough to deliver weapons to their intended targets on distant continents. This military need gave birth to intense effort in both the U.S. and the U.S.S.R. to produce more powerful jet and rocket fuels. Attention focused on the high-energy density fuels and boron hydrides were one of them. Massive, top secret government programs were set in motion to manufacture large quantities of boron-based fuels, and to develop new and better ones. The U.S. Army launched Project HERMES in the late '40s; in 1952 the U.S. Navy Bureau of Aeronautics started Project ZIP; and, in 1956 the U.S. Air Force sponsored Project HEF (High Energy Fuels).

Throughout the 1950s, these programs pushed forward at a tremendous pace, mobilizing many gifted scientists and engineers, all working under a veil of secrecy. At least five boron fuels production plants were built in the U.S., requiring heroic efforts by those involved in handling these dangerous materials. Many problems were tackled along the way, but not without exacting a price, both in terms of money spent and lives lost - two workers were killed in an explosion that destroyed one plant in New York, and tragic fatalities occurred at other sites as well.

News reports of the 1950s conveyed electrifying rumors about boron fuels. Many at the time believed that the Russians used boron fuels to launch Sputnik in 1957. U.S. Borax made news as a material supplier in the race to make full-scale boron fuels a reality. And the U.S. government launched a major project in 1955 to build a boron-fuel-powered long-range strategic bomber called the Valkyrie XB-70A.

Ultimately, the era of boron fuels came to a close. By the end of the 1950s, new generations of jet engines and new fuels involving liquid hydrogen and hydrazine made boron fuels obsolete. Technical problems with boron fuels - including byproducts that decreased engine function and high fuel consumption rates - had proved too hard to overcome.

4. Why Boron ?

The case for boron as fuel begins with a safety advantage. Although very combustible, it also is very hard to ignite. Risk reduction through the use of this fuel that won't burn can be realized if combustors provide an unearthly environment where it will: pure oxygen, high pressure. Hard though this may be, it will yield other benefits.

4.1. High Energy Density

It has high energy density, per pound and especially per gallon. A chamber for it plus a bin for all the glass ingots it would produce together be not much larger than the liquid hydrocarbon tank they replace. The compact energy source and the release of energy at high temperature will make good power to mass ratio, which means quickness in boron motors.

4.2. Where has Boron been Hiding??

Although decades ago programs to use boron as motor fuel began and ended, the method of burning pure solid boron is very different from those programs and treats things that troubled for them as opportunities.

Shortly after the second world war much work was done in the U.S.A. to put boron to work as a military jet fuel by making liquid compounds of it. These compounds were boron-hydrogen compounds, boranes, and compounds of boron, hydrogen, and carbon, known as carboranes.

Some of them are hypergolic in air, i.e., they light on contact with it, and don't need a spark.

Elemental boron is not considered to be toxic. In its pure crystalline form it is chemically inert. It does not dissolve in water, nor in boiling hydrochloric acid.

These compounds were found to carry, much more energy than hydrocarbons. But some problems turned up. According to UCLA (University California and Los Angeles) chemistry professor M. Frederick Hawthorne, "... it was found that you just could not make a turbine engine strong enough to stand up to the boron oxide and boron carbide products of combustion formed from the fuels ..."

Reinterpreting solid boron's ignition resistance as a safety advantage makes one of those difficulties go away. Boron will burn, but not just anywhere. This means the extra chemical synthesis steps a motor fuel plant would have to do to make boranes or carboranes, instead of pure boron, are better left undone.

This change of viewpoint prevents the production of the boron carbide. Hawthorne mentions, if indeed it was ever produced. It is a very hard, motor-eating abrasive. By not making carboranes, we're clear of that problem.

The thing about boria that made it bad for jet engines of the 1950s, and makes it good for us, is its high temperature stability as a liquid.

In the flame that forms it, boria is a very hot gas. But a short distance downstream the flame it condenses to droplets of very hot liquid, and these stick to metal surfaces and don't blow easily out, the way products of hydrocarbon combustion do.

The jet motors were envisioned as propelling long-range bombers, and (one would hope) the demand for propulsion energy for these is always a very small fraction of the total energy demand. So there was no reason to fear the jets could create a scarcity of boron. If the combustion products wanted to stay with the motor, this was just a big nuisance.

We however want to satisfy a very large fraction of the world's future demand for heat in mobile heat engines with boron-oxygen flames. Conceivably these flames could run the world short of boron. An oxide that is easy to retain is just what we want, because we want to keep control of it, and recycle it.

Ash in boron (Diboron trioxide, B_2O_3 . Other names include boron oxide and boric oxide and anhydrous boric acid or boric anhydride) cars would start out as similarly lustrous, transparent ingots. They wouldn't be thrown anywhere, rather, they would go back to nuclear or solar power plants to be de-burnt. Boron Decomposition proposes a thermal method. The boron would be sent forth to be fuel again.

5. Boron: The Energetic Fuel

The following table tells us how much (in kilograms) of several

elements of low atomic number must be oxidized to yield a gigajoule.

Table : 1

Fuel	Molecular weight	Weight of fuel in Kg
Hydrogen	1	8.82
Beryllium	4	15.56
Boron	5	18.30
Carbon	6	30.45
3-ethyl-3-methyl pentane	114	21.9
Aluminum	13	34.10

Reference : CRC Handbook of chemistry and physics, CRC press, Florida, 63rd edition.(1983)

With respect to the weight required to produce a gigajoule of energy hydrogen, beryllium and boron are better than typical hydrocarbon carbon fuel.

6. Boron: The Oxygen Sparing Fuel

When we produce energy by fuel oxidation, we are also producing it by oxygen reduction. Some fuels reduce more kilograms of oxygen per gigajoule yielded, and some fewer. Data follow.

Table : 2

O ₂ (Hydrogen)	1	69.99
O ₂ (Lithium)	3	28.46
O ₂ (Beryllium)	4	27.63
O ₂ (Boron)	5	40.62
3-ethyl-3-methyl pentane		76.68
O ₂ (Carbon)	6	81.13
O ₂ (Magnesium)	12	28.12
O ₂ (Aluminum)	13	30.33
O ₂ (Silicon)	14	37.36
O ₂ (Phosphorus)	15	58.75

Reference : CRC Handbook of chemistry and physics, CRC press, Florida, 63rd edition.(1983)

From the table it is clear that boron reduces almost 50% lesser oxygen as compared to carbon and typical hydrocarbon fuels for the same amount of energy produced.

7. Energy-Specific Ash Mass

Following are the kilogram amounts of oxide produced by complete oxidation of a gigajoule's worth of various substances. The space these oxides might be packed into is given in the section Ash Volumes.

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Table : 3

Hydrogen	1	78.81
Lithium	3	53.16
Beryllium	4	43.19
Boron	5	58.92
Carbon	6	111.58
Magnesium	12	70.84
Aluminum	13	64.44
Silicon	14	70.15
Phosphorus	15	104.24

Reference : CRC Handbook of chemistry and physics, CRC press, Florida, 63rd edition.(1983)

Hydrogen's entry here shows that it isn't the lightest of oxidizable fuels if the weight of necessary oxygen is considered.

8. Ash Volumes

Following table gives volume in litres of oxide formed by combusting amount of fuel required to get a billion joule of energy. The masses of these amounts of oxide are given in the section Energy-Specific Ash Mass.

Table : 4

Hydrogen	1	79.04
Lithium	3	26.41
Beryllium	4	14.35
Boron	5	23.1
Carbon	6	158.1
Magnesium	12	19.77
Aluminum	13	16.16
Silicon	14	26.49
Phosphorus	15	43.6

Reference : CRC Handbook of chemistry and physics, CRC press, Florida, 63rd edition.(1983)

9. Let your Car Bore on

How big are the tanks, really? Answers are given here in terms of litres per three gigajoules, not one, because 1 GJ of fuel energy propels a typical car only about 300 km, and 1,000-km range is not very unusual.

Table : 5

Hydrogen	1	373.8
Methanol	3	177.3
Boron	5	139.9
Carbon	6	55.53
Magnesium	12	199.7
Aluminum	13	132.4

Reference : CRC Handbook of chemistry and physics, CRC press, Florida, 63rd edition.(1983)

The 140-L entry for boron is 108 L for ash, 32 L for fuel. This is based not just on tripling the data from Ash Volumes and Boron the Dense but on multiplying them by further factors of roughly 1.5. These extra adjustments allow for imperfect packing of solids.

10. Convenient Storage

Owing to the passivity of Boron its storage is very easy. Under ambient conditions it does not react with water or any of the constituents of air. Hence, it can be stored anywhere for however long it is desired.

11. Boron the Unignitable

Boron's major safety advantage is that it strongly resists ignition. The inertness is usually attributed to the formation of heat resistant oxide film which is characteristic of a metal but is rarely found in case of non metals. Recent experiments carried out on boron show absence of these films : Boron at room temperature is inert to water but boron oxide reacts with water and the product boric acid dissolves in water. Recent studies show that the oxide layer is never formed at any temperature. They report experiments where electrically heated boron filament would absorb oxygen but not burn even if held in air at a temperature of bright orange incandescence. A little hotter and it would seem to react suddenly with that oxygen, and burn with more from the air around it.

12. How Boron would be used ?

12.1 Combustion in Boron Engine

The internal combustion engines are the chief source of pollution because the combustion products are generally oxides of sulphur, nitrogen and chiefly carbon, which is not the case with boron because being burnt in pure oxygen it does not produce any amount of nitrogen oxides and the fuel being boron it produces boria.

12.2 Internal Boron Combustion Engine Considerations

The very high temperature of the boron-oxygen flame makes it very luminous. Rather than letting the light fly all the way to the combustion chamber walls, it will probably be beneficial if the motor quickly causes the energy to be transferred to the working fluid. This might happen through the fluid absorbing the light, or through its being promptly mixed with the flame, taking the energy by thermal conduction before it can be emitted as light.

The thermodynamic cycle now envisioned is a nearly closed one. Pure oxygen and boron are injected, and pure boria is drawn off. This means oxygen must be separated from air.

A filter using hot metallic silver seems like one possible way to do this. Under pure oxygen at one bar, 0.1 MPa, of pressure 20 volumes of oxygen can be taken up by one volume of liquid silver. Oxygen-laden liquid silver spits as it freezes because the solid can't accommodate as much. But it still takes a lot, as is illustrated by the phenomenon of "firescale", in copper-silver alloys. When they are heated in air, oxygen finds its way through the silver to oxidize copper far below the surface, and the copper oxide heaves up bumps in that surface.

Oxygen must not only go into silver but be forced through it with a pressure gradient. This silver filtration will take power, more research is needed to determine exactly how much, but oxygen purification, by this means or some better one, is essential to an internal boron combustion motor.

13. Characteristics of Boron Combustion

1. all the fuel burns
2. as nothing else is present nothing else burns
3. almost nothing but dense precipitated ash comes.out.

14. Oxygen for Combustion

The crudest oxygen pure boron can readily ignite in is not as dilute as air, 21 percent, but still may be substantially below 99 percent. Although it might light pretty well in 70 percent oxygen, compelling advantages of economy and cleanliness are gained if the purity is much nearer 100 percent. The self-powering, self-propelling oxygen purifier with its hydrocarbon motor replaced with a boron one could apportion a gigajoule of motor output thus: 330 MJ for the purifier, 670 MJ for the wheels.

15. Oxygen Purification based on its Paramagnetism

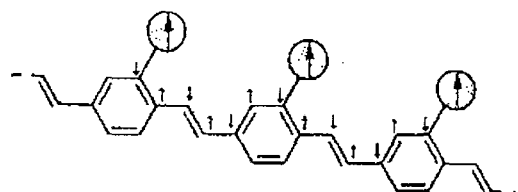


Fig. 1 Cobalt Atoms Magnetically Aligned on Polymer Backbone

Oxygen is the only common substance in air that is weakly attracted by a magnet. Other gases are weakly repelled.

Polymers have been made experimentally that contain rows of aligned tiny magnets — cobalt atoms. These rows act as corridors that hinder the motion of oxygen molecules in directions not parallel to the polymer chain. Other types of molecule will diffuse in all directions, but dioxygens will hop along the polymer backbone.

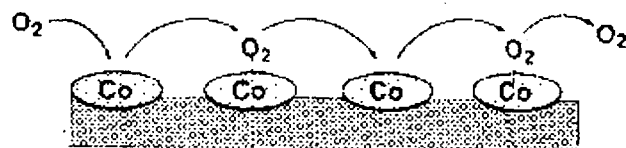


Fig. 2 Oxygen Molecules Getting Magnetically Attached to Cobalt Atoms

The diffusion rate of oxygen is claimed to be 40 times that of nitrogen. That means two stages of filtration through this material would give adequately pure oxygen for a boron motor. The first stage would raise the ratio of oxygen to nitrogen from the 0.26825 that exists in air to 10.7, and the second would raise it over 200.

16. Ash in boron

Ash in boron cars would start out as similarly lustrous, transparent ingots. They wouldn't be thrown anywhere, rather, they would go back to nuclear or solar power plants to be de-burnt. Boron Decombustion proposes a thermal method. The boron will be sent forth to be fuel again ... and again, and again, and again. The oxygen released in the process can be made use of as a fuel. But what with oxygen's being a gas that if kept would have to be kept in something, and the hazardous nature of compressed or liquid oxygen, and the large amount involved — 2.22 kg for each kilogram of boron — new oxygen turns out to be a lot less trouble.

The best thing to do with the oxygen, really the only thing, is store it in the Earth's atmosphere.

One can never get away with discharging boria as smoke. The particles would quickly combine with atmospheric water vapour and become boric acid particles. Boric acid is soluble, and like oxygen can enter the bloodstream through the lungs. In small quantities it may be necessary to animal life, and is definitely harmless, but the tonnes per day that could be generated at a busy urban intersection would be intolerable if dispersed there.

17. Boron Decombustion

It is carried out in the following steps.

17.1 Sulfur

Reagents	Products	ΔG° /(kJ/mol)
<p>First the boria will be melted and have sulfur vapour bubbled through it. Sulfur likes to combine both with oxygen, making sulfur dioxide, and with boron, making diboron trisulfide. Reagents</p> $1/2B_2O_3(l) + 9/8S_2(g)$	$1/2B_2S_3 + 3/4SO_2$	+156.89

If, as seems fitting, this reaction occurs then the two sulfur compounds won't stay together. The sulfur dioxide will stay in the gas bubbles, and the boron sulfide in the liquid, which will become mixed oxide and sulfide.

The positive number in the third column above means that at 25 Celsius the sulfur compounds in the Products column are that much higher in energy than the sulfur and boria in the Reagents one. What could provide the extra energy?

Heat. Sulfur bubbles will be injected at the bottom of a vat of liquid boria that will start out hot, around 1,000 Celsius. As they rise through the liquid the bubbles will lose sulfur to it, take oxygen from it, and even if the vat is well insulated, the whole mixture will cool. Heat will have been transformed into chemical energy.

If this continues the liquid will cool and stiffen until bubbles are effectively trapped. Heat from a solar collector or nuclear reactor must be added. When this is done, a continuous countercurrent process is possible: pure boria in at the top, partially sulfided material out at the bottom. Pure sulfur vapour in at the bottom, partially oxidized sulfur out at the top. Constant temperature maintained by constant addition of heat.

17.2 Bromine

Mixed boria and boron sulfide emerging from the bottom of the sulfur percolation vessel will enter another vessel and have another gas bubbled up through them. The gas this time is the halogen, bromine. The boron atoms that lost their oxygen to a bubble now will be taken off as gas in their own turn.

Reagents	Products	ΔG° /(kJ/mol)
$1/2B_2S_3 + 3/2Br_2(g)$	$BBr_3(g) + 6/8S_2(g)$	-56.82

The negative number in the right column shows bromine would consume boron sulfide, converting it to a gaseous mixture of tribromide and sulfur, even if the gases remained mixed with the liquid sulfide, even without any addition of energy.

This treatment dismantles and lifts out all the boron sulfide and leaves the boria alone. So the liquid becomes once again pure boria, not quite as much as first entered the sulfur percolation vessel. It will return there now, along with additional boria to make up the loss.

17.3 Hydrogen Reduction

A hot boron surface can lose heat and gain boron if it is in contact with a gaseous mixture of boron tribromide and hydrogen. This is an established way of growing boron filament:

Reagents	Products	ΔG° /(kJ/mol)
$BBr_3(g) + 3/2H_2$	$B + 3HBr(g)$	+70.92

Since boron is dark brown and hydrogen bromide, hydrogen, and boron tribromide are all transparent, there is an interesting possibility of using intense light directly to heat the advancing boron surface.

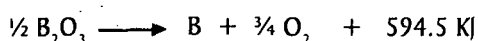
17.4 Conquering the Divided

The sulfur that was combined with boron has already been run out of there by bromine, and so allowed to return to the sulfur percolation vessel. The rest is in sulfur dioxide, which must be broken into its elements, as must the hydrogen bromide:

Reagents	Products	ΔG° /(kJ/mol)
$3HBr(g) +$	$3/2H_2 + 3/2Br_2(g)$	+164.78
$3/4SO_2$	$3/8S_2(g) + 3/4O_2$	+254.99

Reagents		Products	ΔG° /(kJ/mol)
$1/2\text{B}_2\text{O}_3(\text{l}) + 9/8\text{S}_2(\text{g})$	\rightleftharpoons	$1/2\text{B}_2\text{S}_3 + 3/4\text{SO}_2$	+156.89
$1/2\text{B}_2\text{S}_3 + 3/2\text{Br}_2(\text{g})$	\rightleftharpoons	$\text{BBr}_3(\text{g}) + 6/8\text{S}_2(\text{g})$	-56.82
$\text{BBr}_3(\text{g}) + 3/2\text{H}_2$	\rightleftharpoons	$\text{B} + 3\text{HBr}(\text{g})$	+70.92
$3\text{HBr}(\text{g})$	\rightleftharpoons	$3/2\text{H}_2 + 3/2\text{Br}_2(\text{g})$	+164.78
$3/4\text{SO}_2$	\rightleftharpoons	$3/8\text{S}_2(\text{g}) + 3/4\text{O}_2$	+254.99

Leaving out things that are produced in one reaction and consumed in another, and adding up the ΔG° numbers,



18. Challenges

Once pure oxygen is available, it will have to be prevented from burning the motor along with the fuel. New materials of construction will have to be developed for sustaining such a corrosive operating conditions.

A naked boron surface in air can remain naked, or cover itself only with adsorbed air molecules as graphite does. This paradoxically means it may be possible for a suspension of fine boron dust in air to be explosive, like flour or cornstarch. Finely divided boron is very abrasive, so even if it were too coarse to stay aloft it would not be a preferred fuel form.

One could never get away with losing boron as smoke. Boron is a somewhat rare element. In recent years its mining cost has been roughly one order of magnitude more than the retail cost of the energy it can carry. If it made only one trip, boron to deliver a dollar's worth of energy would cost roughly ten dollars. Economy requires the same boron to be used many times. The ash must be kept.

A lot of boron regeneration plants will have to be set up which would require a lot of initial investment.

Efficiency considerations require that oxygen purification be done at high pressure. Pure oxygen and a hydrocarbon polymer could not then safely coexist. One useful development of this technique therefore would be to replace the organic backbone with one that was already full of chlorine, oxygen, or fluorine, i.e. a ceramic, or maybe a halocarbon polymer.

19. Conclusion

In post world war times boron was seen as a potential fuel for long range missiles and bombers but lack of any significant breakthrough diverted the funds to other purposes. Today when we are desperately searching for an alternative fuel boron is envisioned as a potential fuel. Extracting energy from boron by oxidation has many advantages; most of them lie in its passivity. Boron is seen not as a main fuel but it is expected to act as a medium to serve to use energy from nuclear and solar energy which can not be used directly for the automobile application. Today boron is in its early stages of development. It requires a lot of research in the field of thermodynamics, and separation technology for use of boron as a fuel on large scale. The future seems promising and it can be expected that boron will certainly help us meet the ever increasing energy demand while not disturbing the ecological balance.

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