

Flame Retardant Performance of Halogen Free, Alumina Trihydrate Based Bulk Molding Compound

By

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Abstract

Decabromo-diphenyl ether (deca-BDE) and alumina trihydrate (ATH) are both studied separately and together in BMC formulations that are compared with respect to cone calorimetry and NBS smoke chamber results. These results are related to the difference in mechanisms of flame retardance for the two.

BMC formulations based on deca-BDE do give benefits with regard to decreased peak rate of heat release (RHR) and effective heat of combustion, no benefits with regard to time to peak RHR and time to ignition, and decreased performance with regard to carbon monoxide yield and Dm @ 4 minutes and Dm maximum. However using ATH in conjunction with deca-BDE (ATH/Br) improves performance in all of the above aforementioned parameters except Dm maximum.

On the hand BMC formulations with an increasing weight % alumina trihydrate and, no deca-BDE present, display a linear dependence in the direction of goodness on the time to ignition, peak RHR, time to peak RHR, effective heat of combustion, and carbon monoxide yield. Smoke chamber results show reduced specific optical density, Dm @ 4 minutes and at Dm maximum.

The 100% ATH formulas matched or exceeded the ATH/Br based formulas in all quantities measured except the effective heat of combustion. Whether or not this is a particularly important result would need to be determined by the formulator with regard to the flame retardant testing that is dictated by the application.

Introduction

One of the most widely used flame retardants (FR) on the market today is deca-bromodiphenylether (deca-BDE). This FR was to be eliminated from any new EEE (electrical and electronic equipment) by the European Directive, Restriction of Hazardous Substances (RoHS), beginning July 1 2006. However the European Union retracted the ban on October 15, 2005, citing "at present

no need for measures to reduce the risks for consumers beyond which are applied already" [2]. However this exemption can be amended on the basis of new evidence and irregardless, each exemption has a required 4 year review.

The concerns the environmental community has with polybrominated diphenyl ethers (PBDEs) can be traced to their resistance to biodegradability coupled with a tendency for bioaccumulation. These traits classify them as persistent organic pollutants (POPs) [3]. Although the more highly brominated deca and octa versions show less tendency to bioaccumulate as compared to their penta and tetra analogues it is believed that the deca and octa PBDEs have the ability to breakdown in the environment to their lower brominated analogues [3].

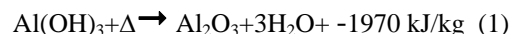
PBDEs have been found in human blood, fatty tissue, and breast milk. Of greatest concern are the developmental and long term exposure effects to children. Indeed biochemical effects, specifically those that cause changes to learning and memory functions which are observed with polychlorinated biphenyls (PCBs); similarly have been observed in work with PBDEs [4]. All of the above point to a very uncertain future for PBDEs. Therefore it is believed prudent for the Composites Industry to develop alternative approaches in achieving acceptable FR performance without the use of PBDEs and specifically, in the context of this paper, deca-BDE.

Background

Flame retardant Mechanism of ATH

It is important to know that when any polymer burns it first pyrolyzes, and then releases low molecular weight flammable gases, which in turn are oxidized by oxygen above the surface of the polymer. This oxidation generates heat, which causes further pyrolysis and so on. Therefore the fire sustains itself. Two important ways flame retardants can act are either in the solid phase as in the case of ATH, or in the gas phase as in the case of halogens such as Bromine (Br).

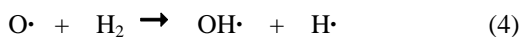
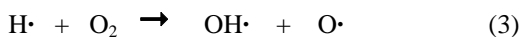
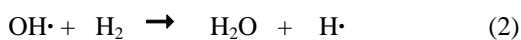
The flame retardant mechanism of alumina trihydrate primarily involves the endothermic decomposition which releases water as shown below:



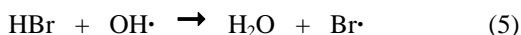
The decomposition cools the substrate's surface and decreases the rate of pyrolysis in the solid phase. Decreased pyrolysis in turn decreases the rate of volatile organic compounds migrating into the flame zone where they are readily oxidized by oxygen. Secondary effects such as dilution of burnable gases by water vapor, formation of an inert oxide layer, and impeding diffusion of oxygen into the flame zone have also been cited.

Flame retardant Mechanism of Halogens

Somewhat more complex than the ATH FR mechanism, is the gas phase halogen FR mechanism [5].



Reactions (2) through (4) are extremely important in degrading the high molecular weight pyrolysis products into low molecular weight volatile compounds. These reactions are very important to the combustion process due to the propagation of the high energy OH \cdot . This radical aids in the decomposition of high molecular weight pyrolysis products into low molecular weight flammable gases. However bromine interferes with this step in the form of hydrobromic acid (in the case of deca-BDE).



The result is the removal of OH radicals from the combustion reaction by HBr as in (5). This cyclic reaction of (5) and (6) is important because OH radicals as mentioned above are responsible for efficient decomposition of the high molecular weight pyrolysis products. This decreases the concentration of volatile, low molecular weight flammable gases, in the flame zone, which readily react with oxygen. Therefore the rate of the combustion process is reduced.

Antimony trioxide (Sb₂O₃) is not a flame retardant but has a synergistic effect with Br. The reaction involves antimony trioxide reacting HBr to produce oxybromide compounds that in turn breakdown into antimony bromide. Antimony bromide is transported into the flame zone where it interferes with the cyclic regeneration of OH \cdot radical.

Particle Packing – Increased ATH loading

The particle packing technique is based on a rheological approach and was used to optimize the ATH components in the BMC tested. The ATH used in this study consisted of coarse and fine fractions, 18.5 micron and 2 micron, respectively. This gives a high MPS ratio of 9.25. The high MPS ratio is necessary in order to achieve workable loading levels \geq 240 parts per hundred resin (phr). In the case of the 280 phr formulation (#14 of Table I) it was necessary to surface treat the 2 micron fraction in order to get a workable viscosity. For details on particle packing in an UPE system the reader is referred to reference 1.

Experimental

A cone calorimeter model CS-237 from Custom Scientific (ASTM E1354) was used to evaluate the time to ignition, heat release rate, effective heat of combustion, and carbon monoxide yield, of the samples. The “cone” was run at a heat flux of 50 kW/m².

A Superpressure-NBS smoke chamber from Newport Scientific (ASTM E662) was used to determine the specific optical density in flaming combustion mode with supporting radiation. Specific optical density, Dm, is recognized as an estimate of the smoke potential of a material. The Dm is reported at 4 minutes, Dm at maximum, and time to Dm maximum.

Median particle size (MPS) measurements were performed on a Cilas Laser Particle Size Analyzer.

A typical neopentyl glycol – isophthalic (NPG-Iso) polyester resin was used for all BMC formulations. The polyester resin, initiator, mold release, and fiberglass (15% by weight) were held constant on a weight basis.

A total of 240 phr was kept constant for the following solid powder constituents when present: deca-BDE/Sb₂O₃, alumina trihydrate, and calcium carbonate. This was done in order to keep the flammable organic phase at a constant mass throughout the study. The only exception was the 280 phr of total ATH used in the highly filled particle packed system. Exact phrs used in each BMC formulation are shown in Table I.

The variable components were (1) ground ATHs with MPS's of 2 and 18.5 μ m, (2) 4 μ m calcium carbonate (CaCO₃), deca-BDE and Sb₂O₃. The deca-BDE and Sb₂O₃ were used at a constant 2:1 weight ratio, respectively, in all formulations. The weight % ATH and Br was calculated on the basis of the weight of paste, and excluding the weight of the fiberglass.

The BMC components were first high sheared into a paste. Lastly a small amount of Mg(OH)₂ was added to the paste to prevent separation of the liquid components, particularly the low shrink additive, high impact polystyrene (HIPS). The paste was then immediately transferred to a bench top Hobart mixer where 15% by weight fiberglass was incorporated. The BMC was allowed to mature for two days before molding. Panels, with dimensions of 12”w x 14”l x 0.125”t, were molded for 3 minutes at ~1,000 psi.

Results

Cone Calorimeter – Deca-BDE containing formulas

Figures 1 through 5 show important quantities, time to ignition, peak rate of heat release (RHR), time to peak RHR, effective heat of combustion, and carbon monoxide yield, plotted against weight % Br (as deca-BDE) for formulations (Table I) containing Br with CaCO₃, #2-#5, and Br with ATH, #6-#9. The CaCO₃ and ATH formulas containing no Br, #1 and #13, respectively, are also included.

Figures 6 through 11 show the same quantities against weight % ATH for the formulations containing ATH only, #10-#14, and the CaCO₃ control (#1) is also included as above.

The CaCO₃ filled formulations, #1-#5, (no ATH) of figure 1 show very little change in time to ignition, ~50-76 s, with increasing Br. A significant increase to ~120 s is noted with the addition of ATH.

In figure 2 the CaCO₃ filled formulations are in a downward trend in the peak RHR as wt. % Br increases and appears to bottom at 250 kW/m² and increases slightly at the highest Br level. On the other hand in the ATH filled formulas no significant decrease in peak RHR is seen with increasing Br. Indeed it would appear that a limiting value of ~175 kW/m² has been reached. It is interesting to note that the 100% ATH formula (#13, without Br present) the peak RHR has about the same peak RHR as the ATH formulas containing Br.

Figure 3, time to peak RHR, shows a relatively short peak RHR time, ~100 s, in the CaCO₃ formulations and changing very little as Br increases. A higher value, ~280s, is achieved by the ATH/Br formulations. However no significant increase occurs with increasing Br. This coincides with the non-effect of increasing wt. % Br on time to peak RHR seen in the CaCO₃ based formulations.

In figure 4 the downtrend in the effective heat of combustion is quite positive for the ATH/Br formulations as wt. % Br increases. Though generally a higher value than in the ATH/Br formulations the same down trend is seen in the CaCO₃/Br formulations, but steeper. Indeed at the highest wt. % Br the average effective heat of combustion is the same for both fillers, ~9 MJ/kg.

Figure 5, the CO yield, shows uptrends in moving from, 100% ATH and 100% CaCO₃ formulations to formulas with increasing Br. At the highest levels of Br the up trend appears to be leveling out in the range of 0.21 – 0.25 kg/kg, respectively. In comparison with the 100% ATH formula this increase in CO yield is ~ 10 fold.

Cone Calorimeter – 100% ATH formulas

Figures 6 through 10 show the same quantities as above but with formulas #10-#14 plotted against wt. % ATH. In figure 6 the time to ignition increases smoothly with increasing wt. % ATH from 54 s in CaCO₃ control to 142s in the 72.6% by wt. ATH formulation, #14. Likewise in Figure 7 the Peak RHR decreases from 390 kW/m² to 160 kW/m². In Figure 8 an increase in time to peak RHR is noted with increasing ATH, from 100 s to 333s. In Figure 9 the effective heat of combustion decreases from 23.7 to 12.6 MJ/kg. It is important to note that this matches the result of formulas #4 (7.81% wt. Br/CaCO₃) and #6 (2.60% wt. Br/ATH). Finally figure 10, CO Yield, shows a decrease from 0.065 to 0.015 kg/kg with increasing wt. % ATH.

NBS Smoke Chamber

The specific optical density, Dm, data is shown in Figure 11. The Dm was recorded at both 4 minutes burn time and at Dm maximum. In comparing 2.6% Br with their 13% Br counterparts, an increase in Dm @ 4 minutes and Dm max is observed with increasing Br. Furthermore the time @ Dm max decreases with increasing Br.

At both 2.6% and 13% Br levels a decreased Dm @ 4minutes is observed in all ATH filled formulations. However Dm max shows very little decrease and at the highest level of Br, 13% by wt., an increase in the ATH filled system. The time to Dm max also decreases with increasing Br when comparing the CaCO₃ and ATH based formulas with each other. The addition of ATH increases time to Dm at a constant wt. % Br. However ATH has very little effect on lowering Dm max in any of the Br based formulas.

In the three ATH formulas, 120, 240, and 280 phrs, “no Br present” very nearly the same Dm is recorded at both 4 minutes and Dm max in the ranges of 14–9 and 147-154, respectively. The time to Dm is quite long ~15.5-16 minutes.

Discussion

ATH filled formulations, #10 through #14

It is remarkable that with increasing wt.% ATH and “no Br present” all of the cone calorimeter generated quantities, the time to ignition, peak RHR, time to peak RHR, effective heat of combustion, and carbon monoxide yield, move in directions of goodness in a linear fashion (figures 6-10). The NBS smoke chamber results show reductions in Dm at 4 minutes and Dm max as well as an increase in time to Dm max even at relatively low levels of ATH.

ATH's endothermic decomposition reaction cools the substrate's surface, which is consistent with the observed increase in time to ignition, 54 s to 142 s with increasing wt. % ATH. This increase in ignition time is indicative of a reduction in the rate of pyrolysis of high molecular weight polymers, the first step in combustion process. The reduction in the rate of pyrolysis also increases the time to peak RHR, 100 s to 333 s.

If ATH decomposition decreases the rate of pyrolysis thereby reducing the concentration of the pyrolysis products, then one could expect that smoke and carbon monoxide yield would decrease as observed. This is because the mass balance ratio between the high molecular weight pyrolysis products and OH radicals favors the OH radicals. A relatively high concentration of the OH radicals is important to an efficient combustion process because this increases the production of short chain and low molecular wt. compounds, or the fuel, available for O₂ to react with in the fire zone. Efficient production of readily oxidizable fuel reduces the level of smoke as seen by low Dm numbers and decreasing CO yield, 0.065 kg/kg to 0.015 kg/kg. From the viewpoint of reduced smoke and CO yield a high concentration of OH radicals is positive.

Br/CaCO₃ formulations, #2 through #5

On the other hand in these formulations, the time to ignition changes very little, 59s to 70s, with increasing Br. Correspondingly the time to peak RHR moves from 100s to 113s. This means that the pyrolysis

rate of reaction continues unabated in generating high molecular weight pyrolysis products. The peak RHR and the effective heat of combustion does decrease from 390 to 310 kW/m² and from 23.7 MJ/kg to 9.5 MJ/kg, respectively, as also in the case of ATH, but for a different reason. Interference with the cyclic reaction producing OH radicals reduces the concentration of readily oxidizable fuel in the flame zone. This results in decreased peak RHR and decreased effective heat of combustion. However a higher molecular weight fuel is produced of less volatility that is less efficiently oxidized in the flame zone as witnessed by the increased smoke and CO yield.

Br/ATH formulations, #6 through #9

Not surprising the Br/ATH based formulations, #6 through #9, have improved performance over their non-ATH containing counterparts in all quantities, except Dm max. This agrees with the view presented above insofar that a reduction in the rate of pyrolysis brings about a more favorable balance in the concentration ratio of the pyrolysis products and the OH radicals. A particularly important example of this is the observed reduction in CO yield. However this does not decrease Dm max, but does improve Dm @ 4 minutes.

Conclusions

The rate of pyrolysis of NPG-Iso polyester resin in the solid phase decreases with increasing ATH. This is seen as a linear improvement in the cone calorimeter generated quantities: time to ignition, peak rate of heat release (RHR), time to peak RHR, effective heat of combustion, and carbon monoxide yield. Because the chemistry of the gas phase, specifically propagation of the OH•, remains unaffected, the smoke generation remains low as seen by the NBS smoke chamber results.

In the case of deca-BDE, the cone calorimeter quantities, peak RHR and effective heat of combustion, do improve with increasing Br. However other quantities, time to ignition and time to peak RHR, do not improve with increasing Br but remain essentially unchanged. The CO yield increases. The NBS smoke chamber show increases in both Dm @ 4minutes and Dm max, coupled with decreasing time to Dm max with increasing Br.

Time to peak RHR and time to ignition remain unaffected because Br has no effect on the rate of pyrolysis in the solid phase. However increased smoke generation with increasing Br is the result of Br interference with the rate of propagation of the OH•. This reduces the efficiency of the oxidation process because higher molecular weight, less volatile compounds are released into the flame zone. Indeed these higher molecular weight compounds are in fact the smoke one observes.

The 100% ATH formulas matched or exceeded the ATH/Br based formulas in all quantities measured except the effective heat of combustion. Whether or not this is a particularly important result would need to be

determined by the formulator through FR testing that is dictated by the application. We believe that the BMC formulator by applying the results as presented in this paper would find that a halogen free, ATH based BMC to be adequate.

References

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Biography

G. C. Rex

G.C. Rex has been the recipient of a B. S. degree in Chemistry (1973) from Bowling Green State University, an M.S. degree (1982) and a Ph. D. in Macromolecular Science (1989) from the University of Detroit. He was an analytical chemist at Allied Chemical from 1973-1976, an R&D chemist at Composite Technology from 1976-1982, a Sr. Research scientist at Union Carbide Corp. from 1986-2001, and Technology Leader at Dow Chemical from 2001-2003. Currently he is Thermoset Manager at J. M. Huber's Fairmount GA Technical Center.

Table I
BMC Formulas in PHR and Results

	CaCO ₃					Deca-BDE with CaCO ₃					Deca-BDE with ATH				ATH with CaCO ₃			100% ATH	
	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11	#12	#13	#14					
NPG-Iso UPE	75	75					75				75			75					
High Impact polystyrene (35% solids)	25	25					25				25			25					
t-butyl perbenzoate	1.5	1.5					1.5				1.5			1.5					
Zinc Stearate	4	4					4				4			4					
Sb ₂ O ₃	0	5	7.5	15	25	5	7.5	15	25	0	0	0	0	0					
Deca-BDE	0	10	15	30	50	10	15	30	50	0	0	0	0	0					
ATH, 18.5 micron	0	0	0	0	0	150	145	130	110	40	80	120	160	187					
ATH, 2 micron	0	0	0	0	0	75	72.5	65	55	20	40	60	80	0					
ATH w surface treatment, 2 micron	0	0	0	0	0	0	0	0	0	0	0	0	0	93					
CaCO ₃ , 4 micron	240	225	217.5	195	165	0	0	0	0	180	120	60	0	0					
Mg(OH) ₂	0.8																		
1/4" fiberglass,	15% by wt.																		
Weight % Bromine	0	2.6	3.9	7.8	13.0	2.6	3.9	7.8	13.0	0	0	0	0	0					
Weight % ATH	0	0	0	0	0	65.1	63.0	56.4	47.8	17.4	34.7	52.1	69.4	72.6					
Cone Calorimeter Results																			
time to ignition, s	54	59	65	76	70	119	132	120	120	85	103	111	128	142					
Peak RHR, kW/m ²	390	340	316	251	310	187	179	160	171	301	230	188	174	160					
Time to peak RHR, s	100	100	100	108	113	283	295	297	252	98	215	270	285	333					
Avg. Effective Heat of Combustion, MJ/kg	23.7	17.1	16.9	13.2	9.5	12.4	11.1	10.0	9.0	19.7	17.4	16.1	14.1	12.8					
CO yield, kg/kg	0.065	0.150	0.168	0.230	0.250	0.041	0.056	0.162	0.210	0.043	0.031	0.026	0.021	0.015					
NBS Smoke Chamber Results																			
Dm @ 4 minutes	234	336	---	---	446	34	---	---	191	---	13	---	14	9					
Dm Max.	---	358	---	---	544	303	---	---	623	---	154	---	147	152					
Time @Dm Max. (min.)	---	6.5	---	---	4.5	12.0	---	---	7.8	---	16.0	---	15.9	15.5					

Figure 1. - Time to Ignition
Increasing wt. % Deca-BDE

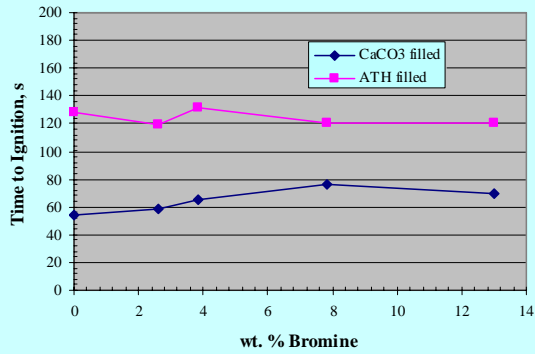


Figure 3. - Time to Peak RHR
Increasing wt. % Deca-BDE

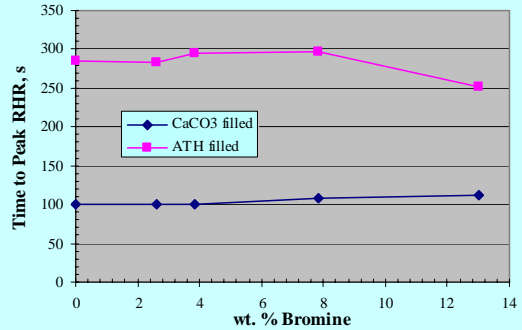


Figure 2. - Peak RHR
Increasing wt. % Deca-BDE

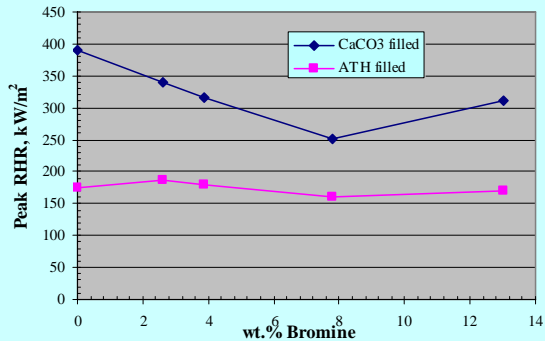
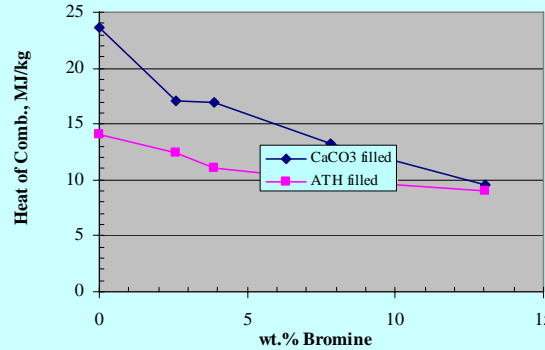


Figure 4. - Eff. Heat of Combustion
Increasing wt. % Deca-BDE



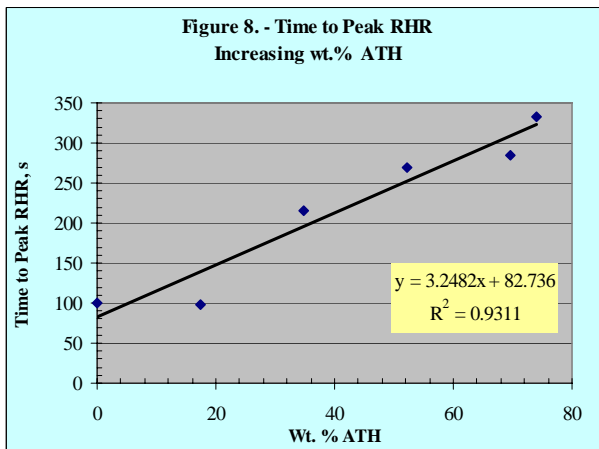
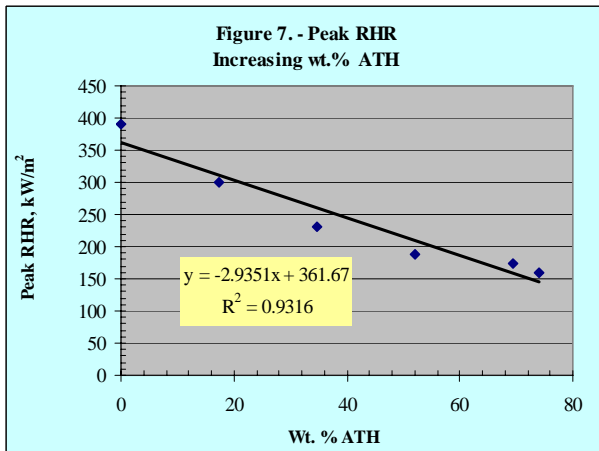
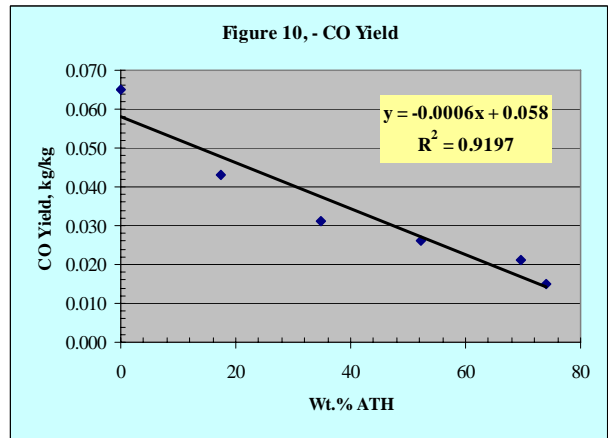
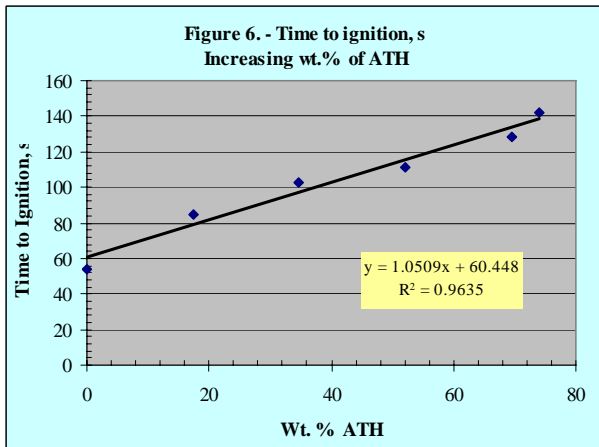
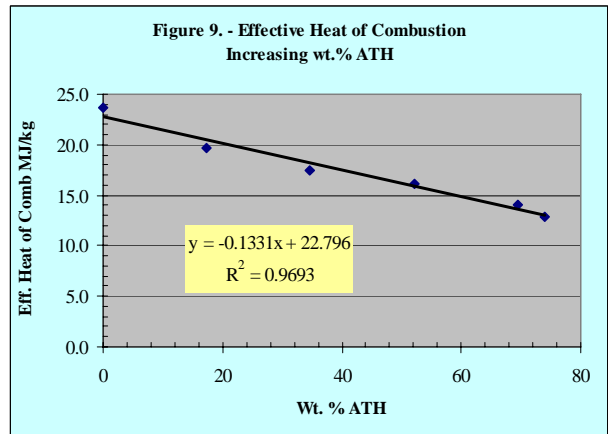
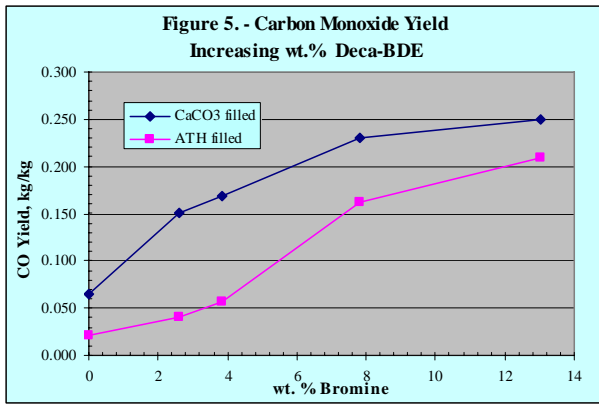


Figure 11. - NBS Smoke Chamber

