Cone Calorimeter Evaluations of *trans*-1,2-dichloroethylene Containing Pentane Foams

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ABSTRACT

Because most of polyurethane insulating foams is used in building construction, they must meet certain fire performance criteria as an individual component as well as a system. For the polyurethane foam industry, it remains to be a challenge to improve fire performance of foam products. In particular, pentanes based polyurethane foams have less desirable fire performance due to the presence of highly flammable blowing agent(s) in the foams.

trans-1,2-dichloroethylene is a liquid at room temperature (b.p. 48 °C). It has no ozone depletion potential[1] (ODP), and it has very low global warming potential (GWP) because it has very short atmospheric lifetime. Previously, we found that the addition of *trans*-1,2-dichloroethylene in pentane based urethane foam formulations significantly improved the surface burning characteristics of the pentane based urethane foams, as evidenced by the reduction in weight loss when subject the foam samples to Mobil 45 small scale fire tests.

To further demonstrate the effect of trans-1,2-dichloroethylene on the fire performance of pentanes based foams, we employed cone calorimeter test (ASTM E-1354). The cone calorimeter test provides peak heat release rate, and heat release rates at various times. Furthermore, the cone calorimeter test offers smoke density generation of the foam samples, which is another important aspect of fire performance. We evaluated urethane foams with 0, 10 and 25 mole% of trans-1,2-dichloroethylene. The results show that the addition of trans-1,2-dichloroethylene reduces the heat release rates, and the smoke density generation2.

INTRODUCTION

In the United States, HCFC-141b had been the blowing agent of choice for the rigid foam applications prior to its phaseout on January 1, 2003. Several zero ozone depletion potential (ODP) blowing agents have emerged as alternatives to HCFC-141b. They can be classified into two categories. One is hydrofluorocarbons or HFCs such as HFC-134a, HFC-245fa and HFC-365mfc. The other category is C5 aliphatic hydrocarbons such as normal pentane, isopentane, cyclopentane and their blends. This transition has posed several significant challenges to the rigid foam industry. One of the most significant one is to meet the fire performance of foam products previously established with HCFC-141b[1]. This is particularly the case for hydrocarbon containing foams because the blowing agent is highly flammable. Achieving certain fire performance rating is necessary for a number of rigid foam applications when they are used in building construction.

Several approaches including uses of fire retardants have been employed to improve fire performance of foams. Yet, it is difficult to achieve desirable fire performance by employing fire retardants alone. Some fire retardants may be effective

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[1] Literature value. However, our internal calculation shows that trans-1,2-dichloroethylene has a negligible ODP. Trans-1,2-dichloroethylene should not be considered as playing a role in ozone depletion and is an illustration of the general conclusion of the WMO 2002 assessment stating the VSL chlorinated substances are not likely to have an impact on the ozone layer.

[2] The numerical values are not intended to reflect hazards presented by these or any other materials under actual fire conditions.

in reducing the flame spread index (or FSI) of foam products. However, they tend to increase the smoke density[2]. For some applications, the foam products must pass both flame spread as well as smoke density criteria. Previously, we found that the addition of trans-1,2-dichloroethylene (or TDCE) can significantly improve fire performance of both pentane and HFC based foams. Using a small scale Mobil 45 test, we found that the presence of 25 mole% of TDCE can significantly reduce the weight loss of foams, compared to foams made with only hydrocarbons as blowing agents[3]. We also found that TDCE can also improve fire performance of HFC-245fa and HFC-365mfc based foams. Using cone calorimeter test (ASTM 1354)[4], we found that the addition of 30 mole% or more of TDCE in 245fa and 365mfc foams can significantly decrease the initial weight loss rate and smoke production[5].

In addition to improve fire performance of hydrocarbon and HFC based foams, TDCE is found to dramatically reduce the viscosity of "B" side blend when used with hydrocarbons, especially normal pentane and isopentane[5]. Moreover, we found that at a level of 25 mole% or less, physical and mechanical properties of resulting foams are acceptable, particularly if it is used with isopentane and normal pentane[5]. Finally, the results showed that the optimum level of TDCE is in between 10 and 25 mole%, within which the fire performance is significantly improved while the aged thermal conductivity is not adversely affected[3].

Because large scale fire tests such as Steiner Tunnel (or ASTM E-84) is costly and requires a large amount of specimens. A number of small scale tests including Mobil 45 have been developed to serve as quick screening tools for foam formulation development. Among them, cone calorimeter (ASTM 1354) test is one of those that can provide both heat release rate (related to intensity of combustion) and smoke generation. Both parameters are important in large scale fire tests.

To further understand effects of TDCE on the flammability of pentane based polyurethane foams, we conduct a study using cone calorimeter (ASTM 1354) to obtain heat release rate and smoke production. The levels of TDCE used in this study are 0, 10 and 25 mole%. The effects of TDCE on the heat release rates and smoke productions of hydrocarbon based PIR foams are investigated.

EXPERIMENTAL

Foam formulations used in this study are listed in table 1. The following is a list of components used in the formulations:

1. PS 2352 (STEPANOL PS 2352) is a polyester polyol produced by Stepan Company. Its hydroxyl number is 230-250.
2. PC-5 (POLYCAT-5) is an amine catalyst produced by Air Products. Its chemical name is pentamethyldiethylenetriamine.
3. PC-46 (POLYCAT-46) is isocyanurate catalyst by Air Products. It is potassium acetate in ethylene glycol.
4. K-15 (DACBO7 K-15) is a metal based catalyst by Air Products. It is potassium octoate in dipropylene glycol.
5. B-8462 (TEGOSTAB B8462) is a polysiloxane-polyether copolymer (or simply called silicone surfactant) produced by Goldschmidt Chemical Corporation.
6. AB80 (ANTIBLAZE 80) is a fire retardant produced by Albright & Wilson Americas, Inc. Its chemical name is tris(1-chloro-2-propyl)phosphate.
7. Normal pentane or n-C5 (99+%) is from Aldrich Chemical Company.
8. Cyclopentane or c-C5 (pure grade, 99.5%) is from Philips 66 Company.
9. isopentane or i-C5 (99+%) is from Aldrich Chemical Company
10. trans-1,2-dichloroethylene or TDCE (99^+%) is from Arkema Inc.
11. M-489 (Mondur 489) is a polymeric methane diphenyl diisocyanate (polymeric MDI) produced by Bayer Corporation.

In this study, all specimens were free rise foams and they were produced using a handmix technique described as follows: "A" side contains polymethylene isocyanates (Mondur 489), and it is maintained at 10 °C. "B" side premix contains polyester polyol (PS 2352), surfactant, fire retardant, blowing agent(s) and additives such as TDCE. The "B" side premix is cooled to 10 °C as well. The predetermined amount of "A" and "B" sides are mixed with a mixer (3500 rpm) for 19-20 seconds. This is followed by the injection of a catalyst mixture (predetermined amount of PC-5, PC-46 and K-15). The mixing is allowed to continue for additional 16-18 seconds before pouring the mixture into a tray. The foam samples are allowed to cure for at least 24 hours before testing.

The fire performance of the foams was evaluated with a cone calorimeter test, according to ASTM E 1354-02d. The thermal flux applied on the specimen surface is 50 kW/m².

Peak heat release rate (Pk HRR), Average heat release rate at 60 seconds, 180 seconds, 300 seconds as well as average specific extinction area or smoke production are reported. The specimens tested have a size of approximately 100 mm x 100 mm with a thickness of approximately 50 mm. Three specimens were used for each formulation, and the results shown are the average of three samples.

RESULTS AND DISCUSSION

In this study, we investigated the effect of TDCE on PIR foams made with normal pentane, isopentane, cyclopentane and a blend of normal/isopentane with about 75% of normal pentane. Foam formulations for normal pentane/TDCE are listed in Table 1. Foam formulations for isopentane/TDCE, cyclopentane/TDCE and normal pentane/isopentane/TDCE (not shown) are similar to normal pentane/TDCE.

For normal pentane/TDCE foams containing 0, 10 and 25 mole% of TDCE, the results are shown in Figures 1-4. Figure 1 shows the peak heat release rate (Pk, HRR) as a function of TDCE levels, the results indicate that the addition of TDCE can significantly reduce the peak heat release rate. At 25 mole% of TDCE, the reduction of peak heat release rate is about 36%. There is also a significant decrease in average heat release rate (HRR) at 60 seconds (after ignition) with an addition of 25 mole% of TDCE. Similar trend is observed for the heat release rates at 180 seconds and 300 seconds, respectively. The data demonstrate that the addition of TDCE reduces the initial intensity of combustion, therefore improves the fire performance of normal pentane blown foams. Figure 3 shows smoke production or specific extinction area (SEA) as a function of TDCE levels. The results indicate that the addition of 10 to 25 mole% of TDCE reduces the smoke production of normal pentane foams by about 20% during the combustion. As shown in Figure 4, the presence of TDCE has little influence on the effective heat of combustion.

For isopentane/TDCE foams with 0, 10 and 25 mole% of TDCE, the results, shown in Figures 5-8, are similar to normal pentane/TDCE foams. Again, there is a very significant reduction (about 37%) in the peak heat release rate with the addition of 25 mole% of TDCE (Figure 5). Overall, the average heat release rates at 60, 180 and 300 seconds decrease with the addition of TDCE, the effect is less significant for the average heat release rate at 300 seconds. Like normal pentane/TDCE foams, the addition of TDCE at 25 mole% significantly reduces the smoke production (by about 25%). Again, the presence TDCE at 10-25 mole% has little effect on the average heat of combustion of isopentane/TDCE foams (Figure 8).

When 25 mole% of TDCE is used in n-C5/i-C5 (75/25) PIR foams, peak heat release rate is reduced by about 30%, as shown in Figure 9. The heat release rates at 60 seconds and 180 seconds are significantly reduced at 25 mole% of TDCE, with less significant reduction of the heat release rate at 300 seconds (Figure 10). As seen in Figure 11, the smoke production is decreased by approximately 25% when 10 mole% of TDCE is used in the formulations. Once again, there is little change in the effective heat of combustion with and without the presence of TDCE (Figure 12). Generally speaking, the flammability behaviors of n-C5/i-C5/TDCE are very similar to n-C5/TDCE and i-C5/TDCE.

For c-C5/TDCE PIR foams, shown in Figures 13-14, the addition of TDCE does not have an effect on the peak heat release rate and heat release rates at 60, 180 and 300 seconds. However, the smoke production (Figure 15) is reduced by about 20% when 25 mole% of TDCE is used in the formulations. The reduction in smoke is consistent with our observations with n-C5/TDCE, i-C5/TDCE and n-C5/i-C5/TDCE. Unlike other series, the addition of TDCE reduces the effective heat of combustion by about 20% when 25 mole% of TDCE is present in the foam formulation (Figure 16).

The significant reduction in the peak heat release rate, heat release rates at 60, 180 and 300 seconds indicates that the initial intensity of combustion is reduced with the addition of TDCE. The results show that the addition of TDCE in pentane based foams improves the fire performance. This is consistent with our previous results that showed that the presence of 25 mole% of TDCE reduces the weight loss of foam samples when the samples are subject to flame in the Mobil 45 small scale fire tests. The cone calorimeter test results also consistently show that there is a significant reduction in smoke production with the presence of 25 mole% of TDCE. The effect of TDCE on the smoke generation is similar to what we previously found with HFC-245fa/TDCE and HFC-365mfc/TDCE foams.

CONCLUSION

For n-C5/TDCE, i-C5/TDCE, n-C5/i-C5/TDCE and c-C5/TDCE PIR foams, there is a consistent reduction in smoke generation by about 20 to 25% when 25 mole% of TDCE is added in the formulations. There is also a significant decrease in peak heat release rate, heat release rates at 60, 180 and 300 seconds for n-C5/TDCE, i-C5/TDCE and n-C5/i-C5/TDCE PIR foams. The results demonstrate that the addition of TDCE in pentane can improve the fire performance of the pentane based foams.

ACKNOWLEDGEMENT

The authors would like to thank Omega Point Laboratory for conducting Cone Calorimeter tests.

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BIOGRAPHIES

Jinhuang Wu is a Senior Research Scientist at Arkema Inc. Technological Center in King of Prussia. He received his PhD in Macromolecular Science and Engineering from the University of Michigan, and joined Arkema Inc. in March 1997.

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John Maxwell joined Arkema Inc after he graduated from Holy Family College with a BA in Chemistry in December 2002.

Table 1. Formulation of normal pentane/TDCE foams

Formulation	#1	#2	#3
STEPANPOL® PS 2352[1]	100	100	100
POLYCAT®-5[2]	0. 24	0. 24	0. 24
POLYCAT®-46[3]	0. 44	0. 44	0. 44
DABCO® K-15[4]	2. 57	2. 57	2. 57
TEGOSTAB® B-8462[5]	2.00	2.00	2.00
Antiblaze® 80[6]	10.0	10.0	10.0
***trans*-1,2-dichloroethylene (TDCE)**	0	3.31	8.27
n-C_5	24.55	22.10	18.41
Mondur® 489[7]	170.51	170.51	170.51
Iso index	300	300	300

[1]Stepan Company; [2,3,4]Air Products; [5]Goldschmidt Chemical Corporation; [6]Rhodia, Inc.; [7]Bayer Corporation

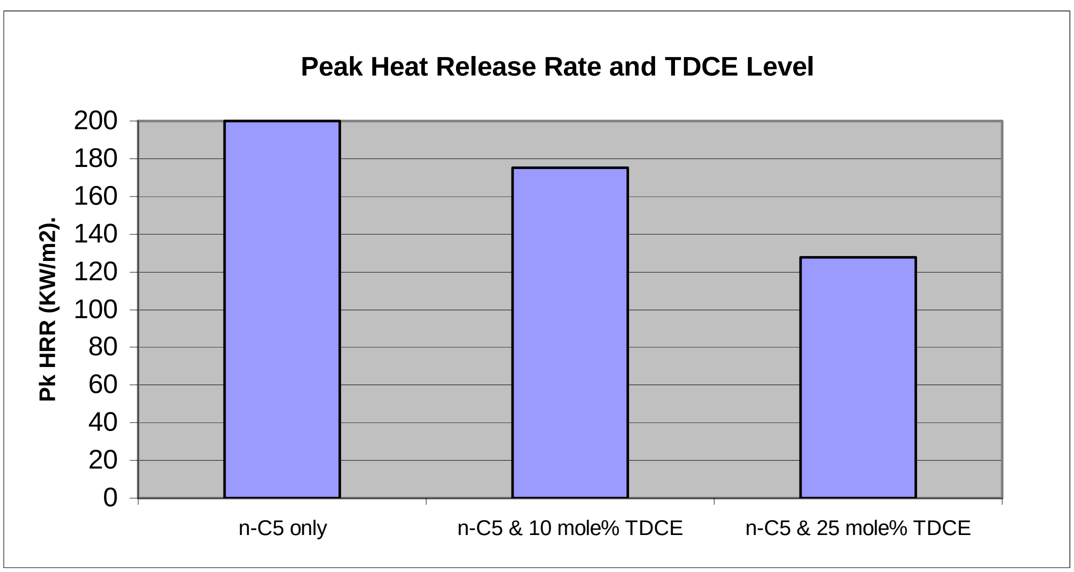

Figure 1. Effect of TDCE level on Peak Heat Release Rate of n-C5/TDCE Foams

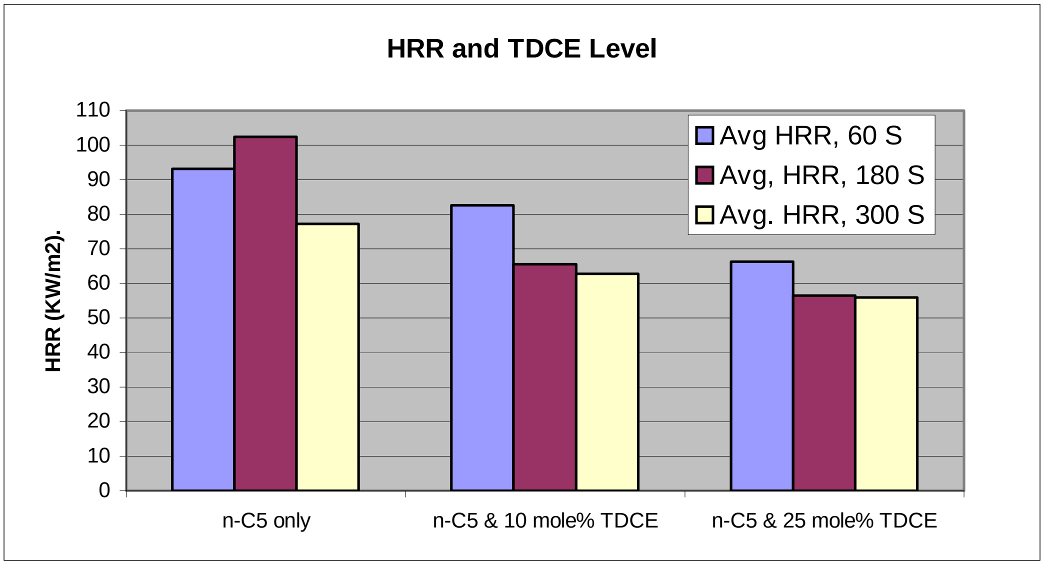

Figure 2. Effect of TDCE level on Heat Release Rate of n-C5/TDCE Foams

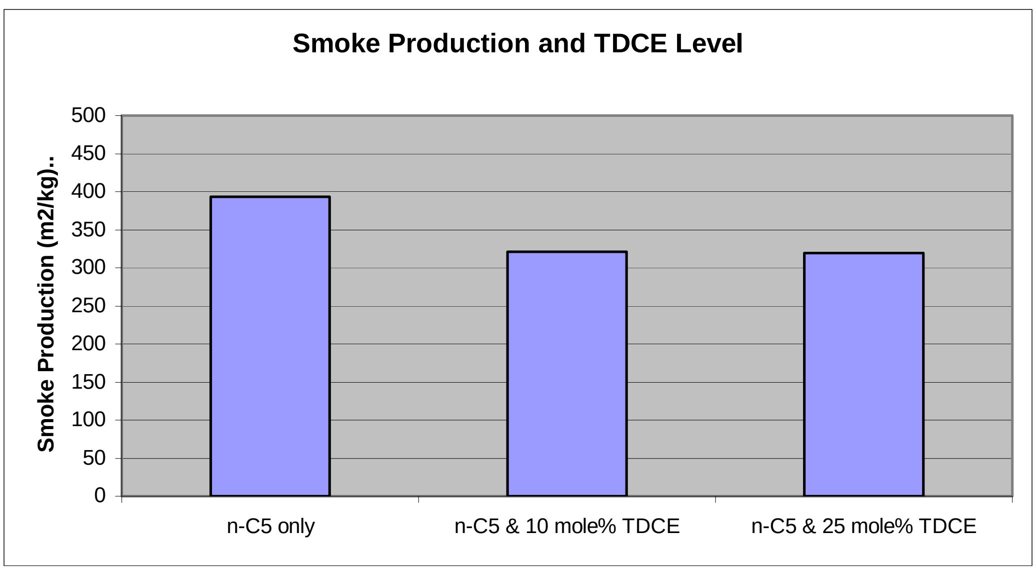

Figure 3. Effect of TDCE level on Smoke Production of n-C5/TDCE Foams

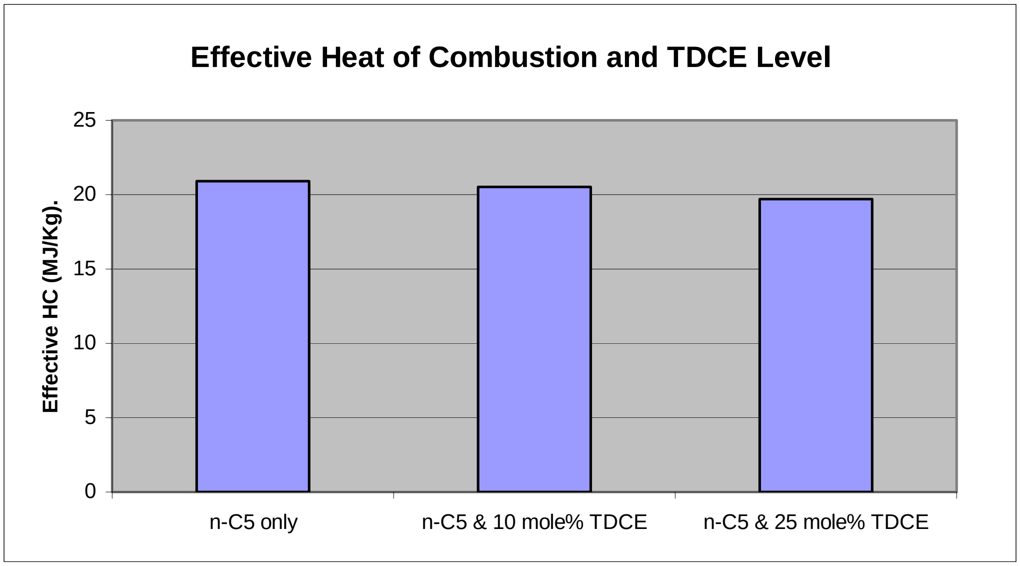

Figure 4. Effect of TDCE level on Heat Combustion of n-C5/TDCE Foams

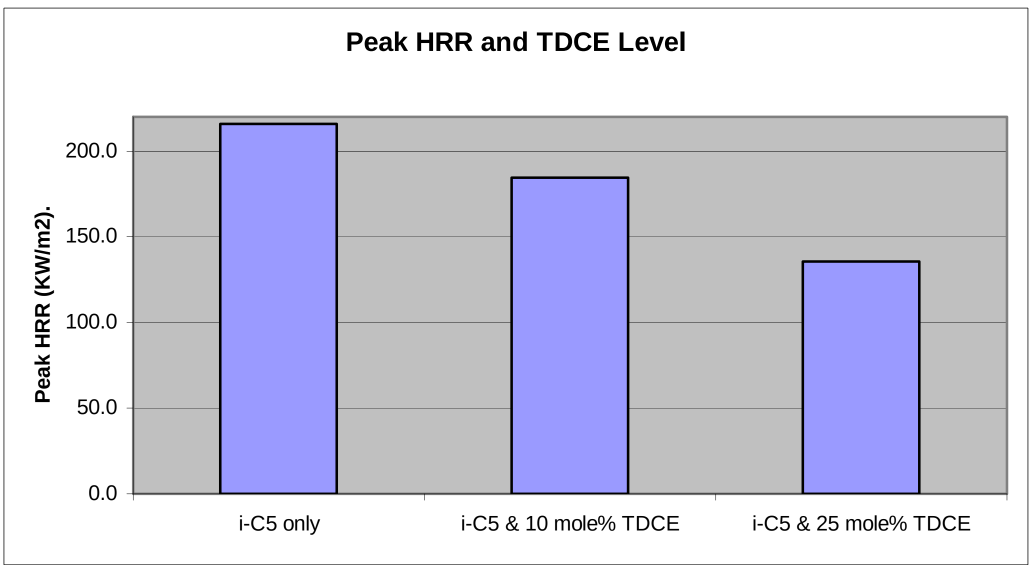

Figure 5. Effect of TDCE level on Peak Heat Release Rate of i-C5/TDCE Foams

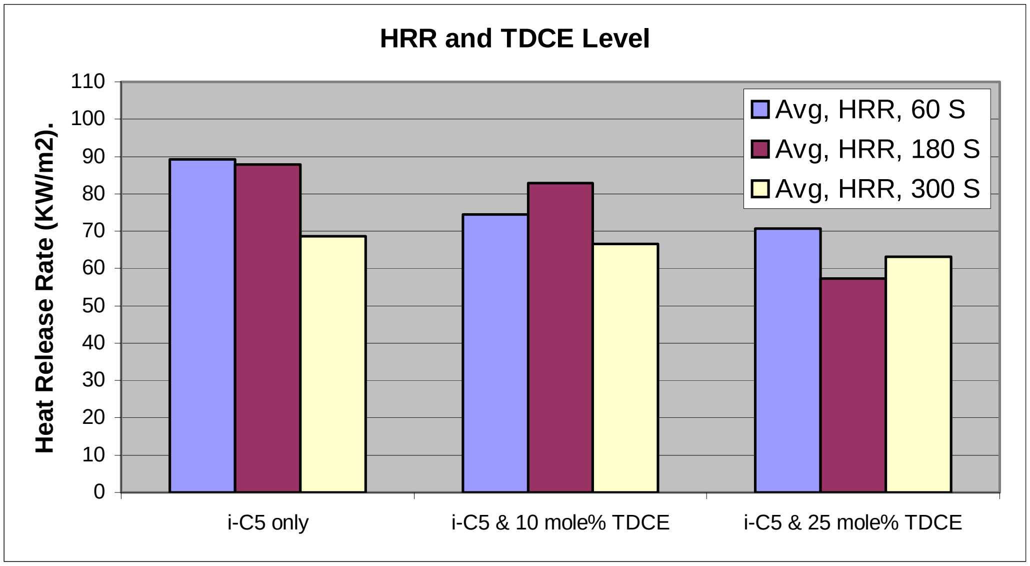

Figure 6. Effect of TDCE level on Heat Release Rate of i-C5/TDCE Foams

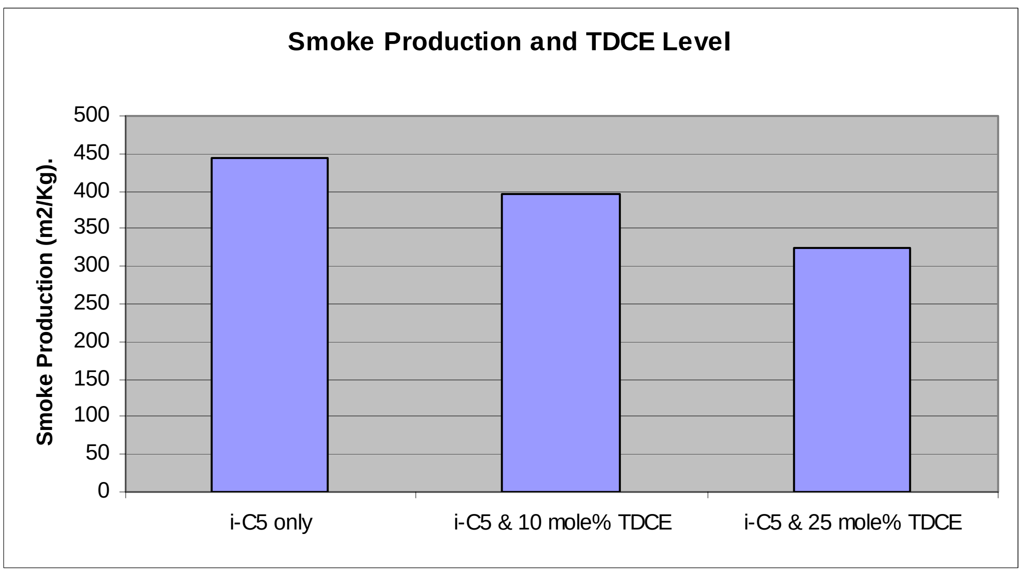

Figure 7. Effect of TDCE level on Smoke Production of i-C5/TDCE Foams

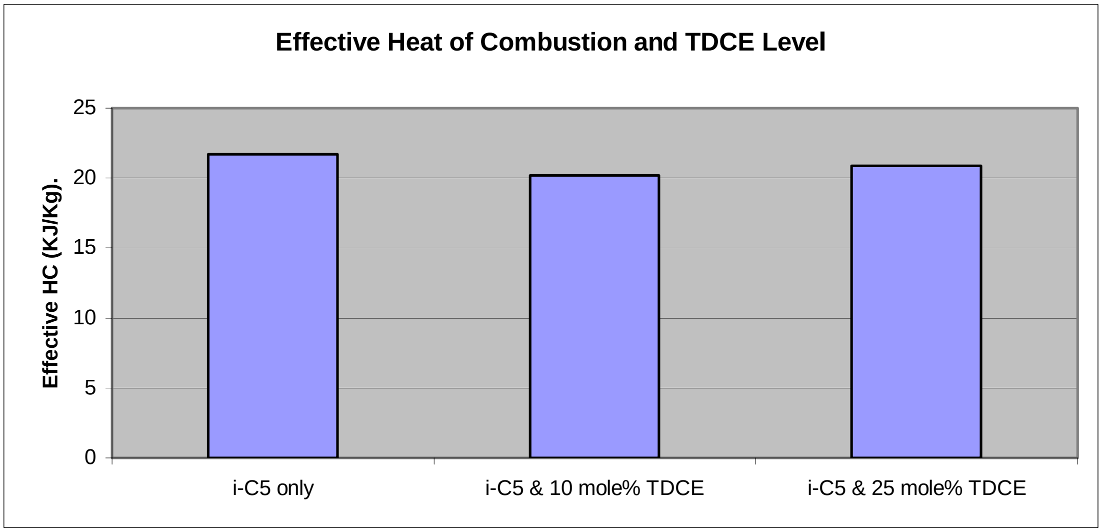

Figure 8. Effect of TDCE level on Heat Combustion of i-C5/TDCE Foams

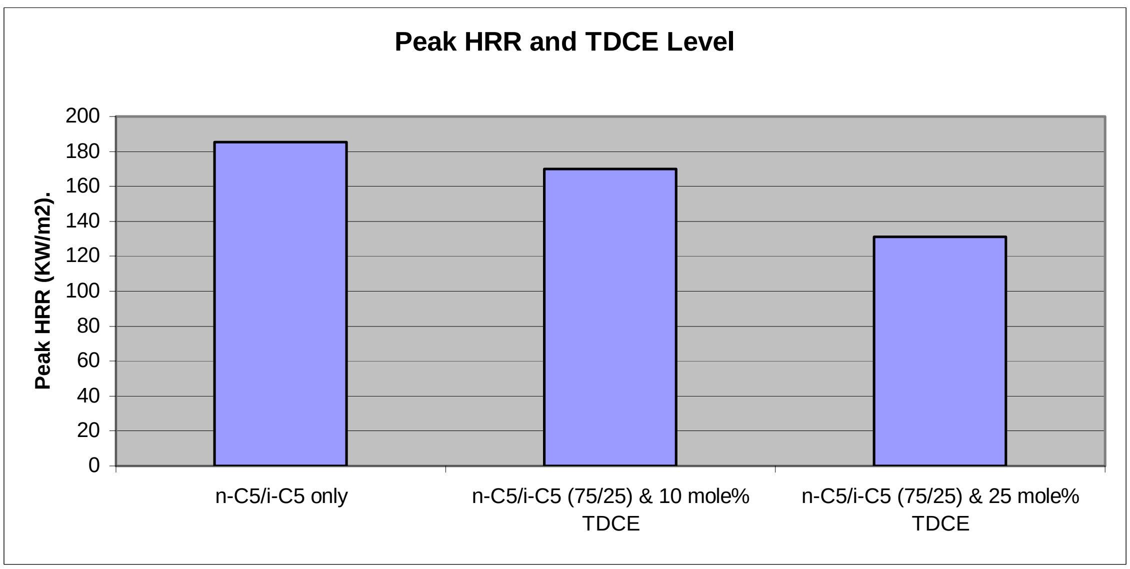

Figure 9. Effect of TDCE level on Peak Heat Release Rate of n-C5/i-C5/TDCE Foams

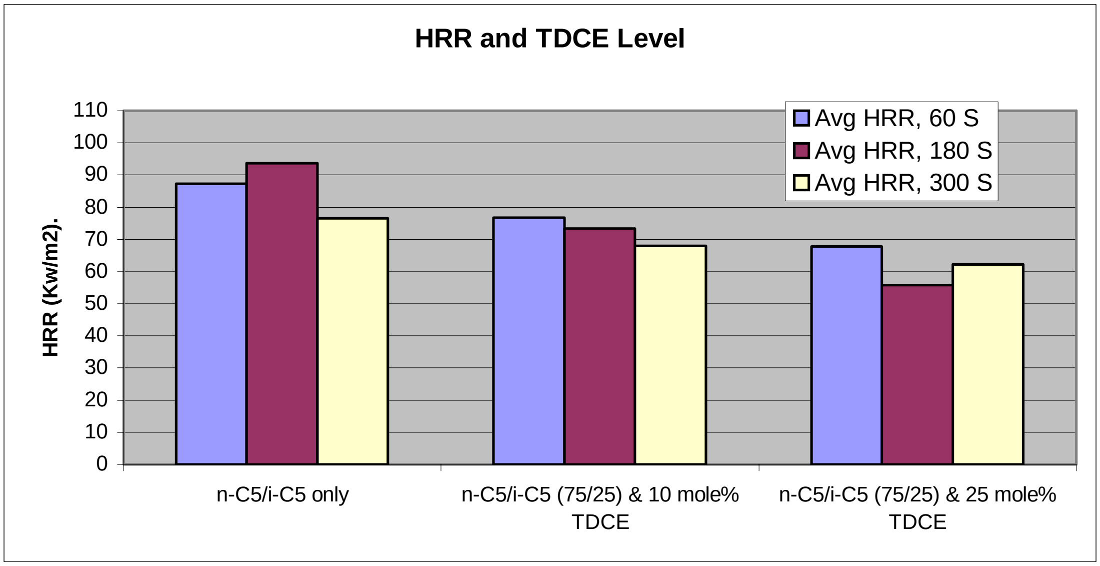

Figure 10. Effect of TDCE level on Heat Release Rate of n-C5/i-C5/TDCE Foams

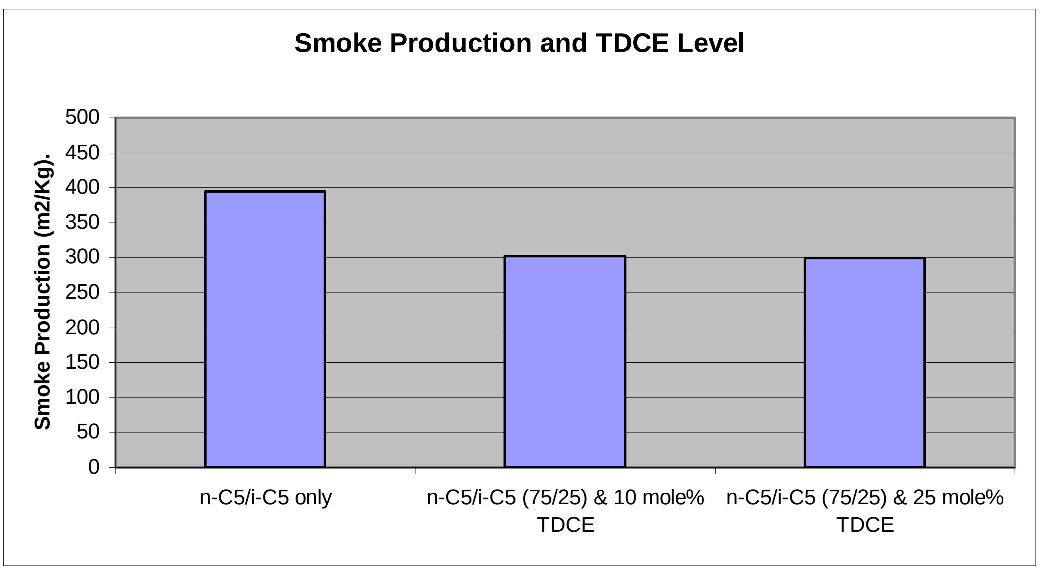

Figure 11. Effect of TDCE level on Smoke Production of n-C5/i-C5/TDCE Foams

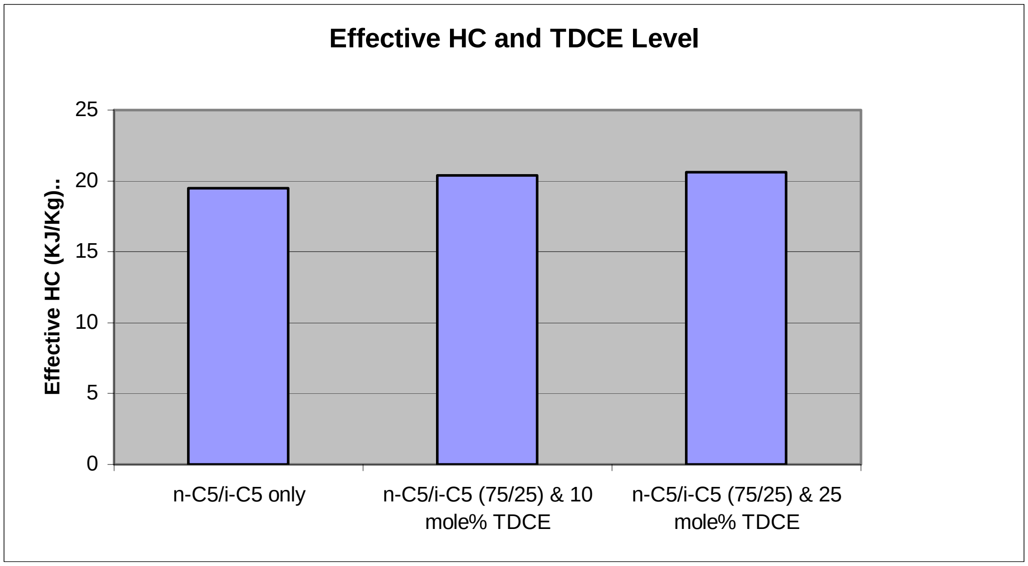

Figure 12. Effect of TDCE level on Heat Combustion of n-C5/i-C5/TDCE Foams

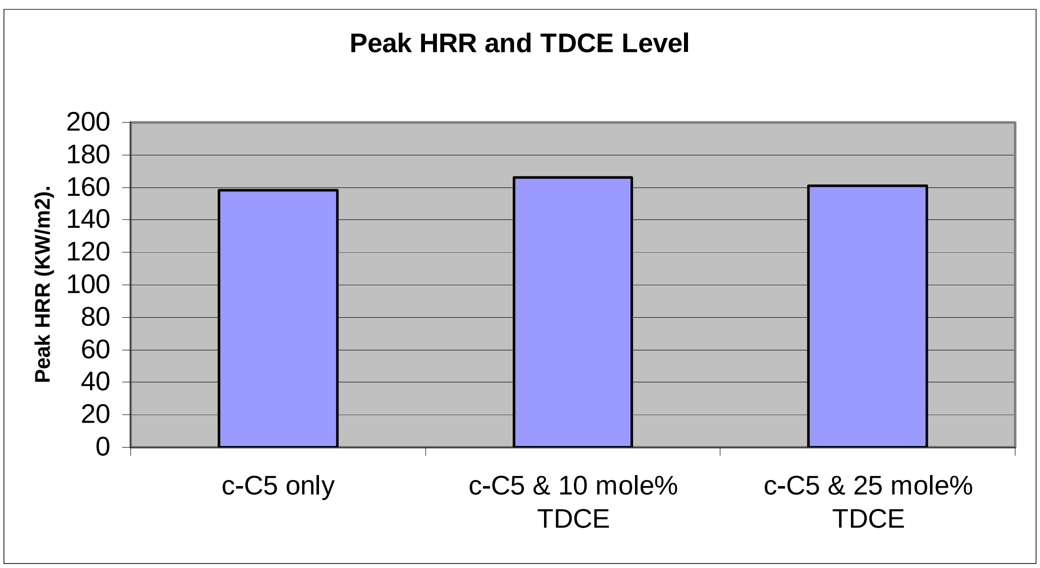

Figure 13. Effect of TDCE level on Peak Heat Release Rate of c-C5/TDCE Foams

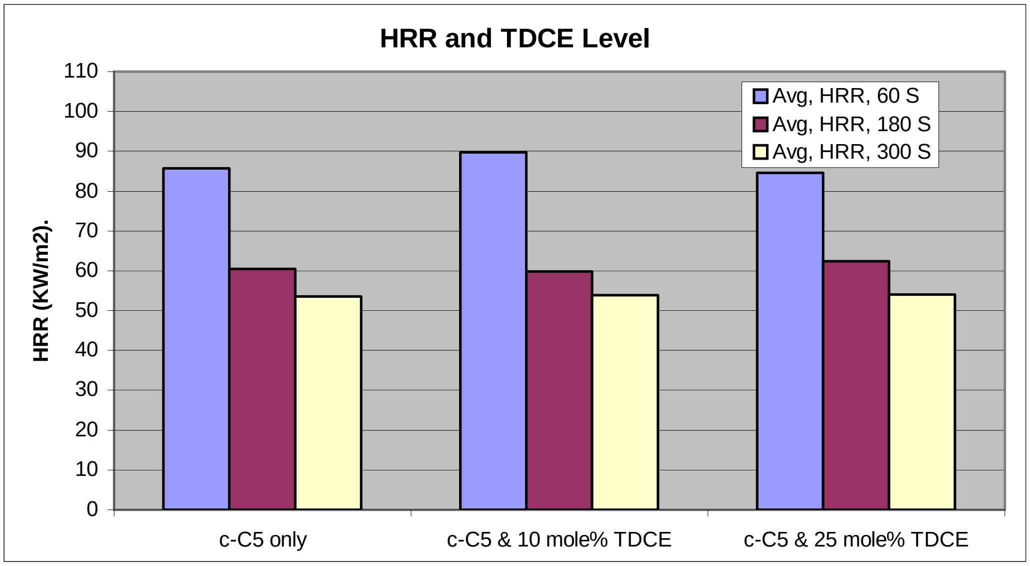

Figure 14. Effect of TDCE level on Heat Release Rate of c-C5/TDCE Foams

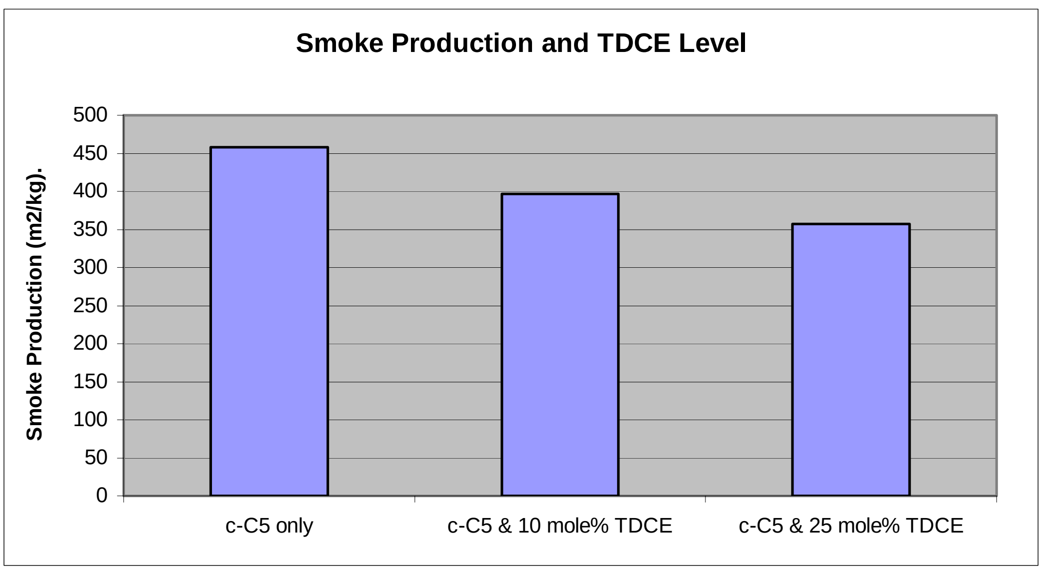

Figure 15. Effect of TDCE level on Smoke Production of c-C5/TDCE Foams

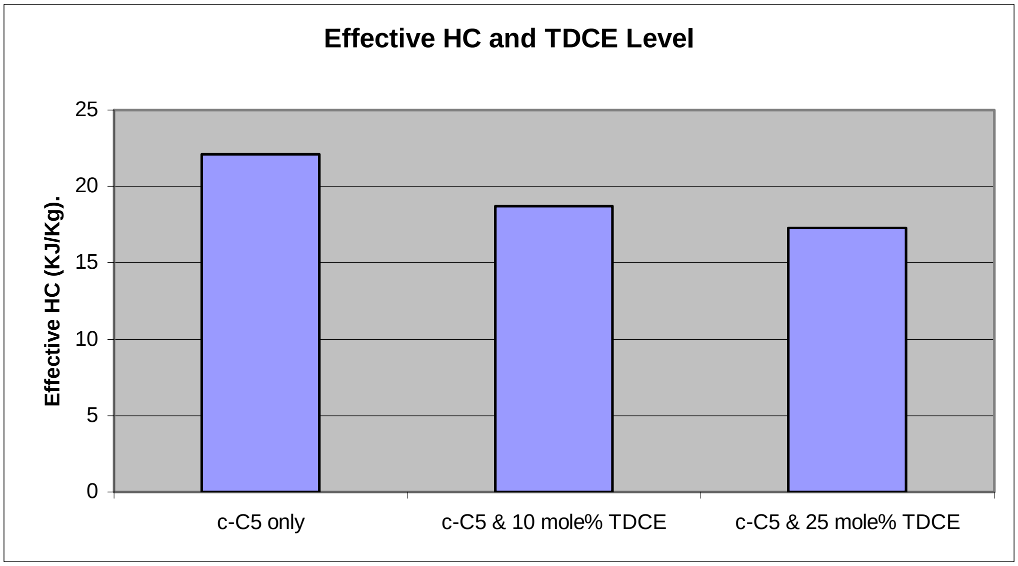

Figure 16. Effect of TDCE level on Heat Combustion of c-C5/TDCE Foams