

LETTER TO THE EDITOR

In a recent paper in this journal, Ewing, Faith, Romans, Hughes and Carhart¹ have presented arguments for the proposition that heat extraction is the principal mode by which dry chemicals extinguish fires. This is at variance with the long-held belief that chemical kinetics plays an important role, especially for potassium salts.

The paper presents new data for extinguishment of heptane pan fires by air containing a controlled percentage of any of various finely ground powders. The authors found that addition of 0.0305 grams of potassium carbonate (K_2CO_3) or 0.04305 grams of sodium carbonate (Na_2CO_3) per liter of air at 298 K was just adequate to cause extinguishment. They then described thermochemical calculations which they believe to be consistent with these numbers. The calculations were based on the assumptions that K_2CO_3 decomposes in the flame to form K (gas), O_2 , and CO_2 , while the Na_2CO_3 decomposes to form Na_2O (liq) and CO_2 , in each case with appropriate enthalpy changes. They found the calculated heat-sink effect of 0.0305 grams of K_2CO_3 per liter of air at 298 K to be essentially the same as the heat-sink effect of 0.04305 grams of Na_2CO_3 . Successful calculations were also presented for other powders, but I limit my discussion to these two.

I believe that their thermochemical calculations are incorrect, because they did not take into account the fact that KOH or NaOH is the primary product when a potassium or sodium salt is introduced into a hydrocarbon flame, or even into hot air containing a small percentage of water vapor.

Using the NASA equilibrium program², I have calculated the compositions of air containing 2 mole percent water vapor and either

0.0305 grams of K_2CO_3 per liter or 0.04305 grams of Na_2CO_3 per liter, at 1900 K and one atmosphere. Results are shown in Table 1.

It is seen that 91 percent of the potassium ends up as the gaseous hydroxide, while 74 percent of the sodium ends up as the gaseous hydroxide. These numbers would be a little different at other assumed temperatures. For example, at 1700 K, 98 percent of the potassium or 91 percent of the sodium ends up as the hydroxide.

I also calculated the equilibrium products at 1900 K of a stoichiometric mixture of propane and air along with 0.0305 grams of K_2CO_3 per liter of air. In that case, as before, 91 percent of the potassium was in the form of KOH.

I then investigated the thermochemical consequences of adding K_2CO_3 or Na_2CO_3 to hot moist air, using the NASA equilibrium program, with results shown in Figure 1. The top curve shows the final temperature of air containing 2 mole percent water vapor, if initially at 298 K, as a function of the enthalpy added. The middle curve is a repeat of this calculation with 0.0305 grams of K_2CO_3 initially present per liter of air at 298 K. It is seen that, for any final temperature in the range explored (1500 to 2100 K), a given enthalpy addition will result in a lower final temperature when K_2CO_3 is present, because of its endothermic decomposition. However, this addition of K_2CO_3 , which is reported to be sufficient to cause extinguishment, lowers the temperature only by 60 to 70 degrees, over the range studied.

The bottom curve shows the result of the calculation with 0.04305 grams of Na_2CO_3

Table 1. Molar equilibrium compositions at 1900 K and one atmosphere of moist air (77.45 % N₂, 20.59 % O₂, 2.00 % H₂O) plus either 0.0305 grams K₂CO₃/liter or 0.04305 grams Na₂CO₃/liter.

	Moist Air + K ₂ CO ₃	Moist Air + Na ₂ CO ₃
KOH	0.957 %	
K	0.084 %	
KO	0.006 %	
NaOH		1.413 %
Na		0.452 %
NaO		0.036 %
N ₂	76.28 %	75.40 %
O ₂	20.07 %	19.92 %
H ₂ O	1.437 %	1.189 %
NO	0.587 %	0.581 %
CO ₂	0.523 %	0.950 %
OH	0.045 %	0.041 %
O	0.013 %	0.013 %
CO	0.001 %	0.001 %
NO ₂	0.001 %	0.001 %
	100 %	100 %

added per liter of air at 298 K. It is seen that this amount of Na₂CO₃ causes a much larger lowering of the temperature than for the K₂CO₃ case, over the range of assumed enthalpy additions. For example, addition of 420 calories of enthalpy per gram of moist air at 298 K is seen to raise its temperature to 1800 K. If the critical extinguishment amount of K₂CO₃ is present, this same addition of enthalpy yields a temperature 62 degrees lower, while the critical amount of Na₂CO₃ yields a temperature 144 degrees lower.

Let us consider these results in relation to the extinguishing mechanism. In the first place, the calculated reductions in temperature caused by endothermic decomposition of the critical amounts of K₂CO₃ or Na₂CO₃ seem to be too small to explain extinguishment. Experiments with inert additives indicate that a temperature reduction of at least several hundreds of degrees would be required.

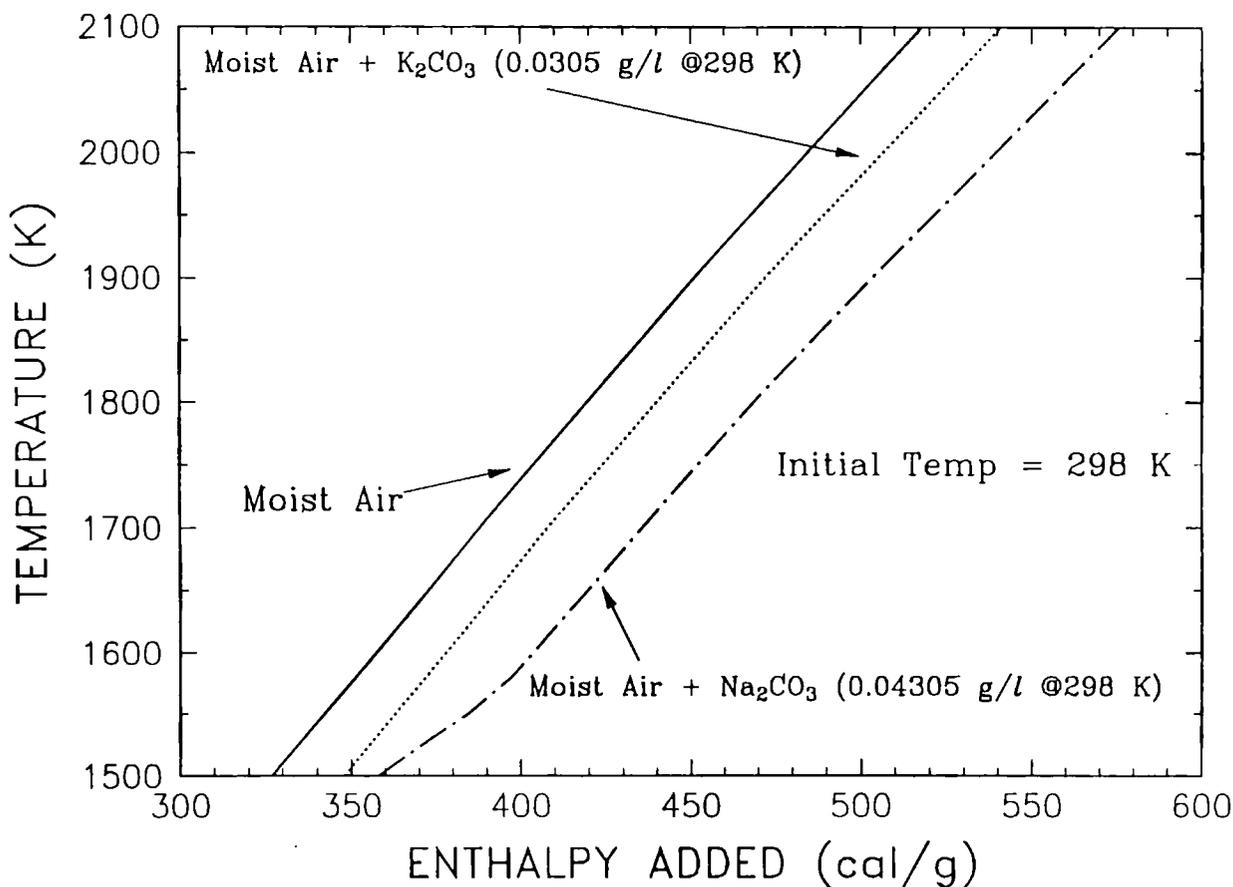


Figure 1. Temperature of moist air plus additives as a function of added enthalpy (NASA equilibrium code).

In the second place, and more quantitatively, the foregoing calculations show that the critical amount of Na_2CO_3 causes more than twice the temperature reduction than does the critical amount of K_2CO_3 , whereas the reduction should be the same in each case if heat extraction is the dominant mechanism.

Finally, I agree with the long-held belief that, for potassium salts especially, the extinguishment mechanism involves chemical reactions between salt decomposition products and flame free radicals. The difference in effectiveness of various salts must relate to chemical kinetic differences as well as heat-sink effects. Of course, the above calculations show that the heat-sink effects are not negligible and should not be ignored.

Acknowledgement

Mary K. Mathews and John de Ris were extremely helpful in the performance of the calculations in this note.

Sincerely,
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REFERENCES

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