Fire gases of rubber materials - a systematic investigation

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Introduction

Fig. 1. *Tire stockpile fire*

Rubber materials are stored in production plants before, during and after the production process or in landfills after use. These stockpiles possess high energy contents (ca. 33 MJ/kg) and occasionally catch fire (*see Fig. 1*). Rubber fires are long lasting and very difficult to extinguish. Large amounts of potentially harmful combustion products are emitted into the atmosphere.

Abstract

In this study fire gases of selected rubbers and elastomers are investigated for their qualitative, quantitative and time/temperature-dependent composition. The main combustion parameters are systematically varied. The used investigation methods, suitable analysis methods and fire gas compositions are presented.

The forecast of fire gas compositions and a hazard assessment of rubber fires are the objectives of the study.

Combustion process

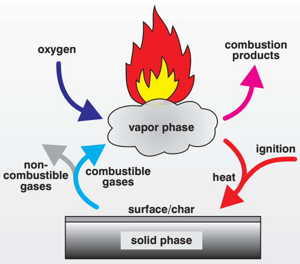


Fig. 2. *Combustion process*

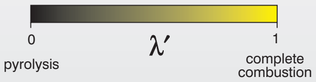
The combustion process is affected by numerous parameters:

- depending on fire load
  - chemical composition
  - mass
  - chemical and physical properties of the surface
  - heat conductivity
  - ignition temperature
- independent of fire load
  - temperature
  - oxygen availability
  - fire environment
  - ignition source

Fire characterization using a modified burn out ratio λ'

$$\lambda' = \frac{O_{2_{rec.}}}{O_{2_{theor.}}}$$

The modified burn out ratio λ' is defined[2] as the ratio of oxygen recovered ($O_{2,\ rec.}$) post-experiment (e.g. as CO, CO_2, SO_2,SO_3) vs. the theoretical oxygen uptake ($O_{2,\ theor.}$) based on the reactions $C \rightarrow CO_2$ and $S \rightarrow SO_3$



Examined rubber materials

Raw polymers

- SBR
- NR
- BIIR
- CR
- NBR
- EPDM

Mixtures and vulcanizates

- passenger tire tread based on SBR 1712
- truck tire tread based on NR RSS3
- innerliner based on BIIR
- axle joint gaiter based on CR

Methods

Fire simulation in the VCI*) combustion chamber

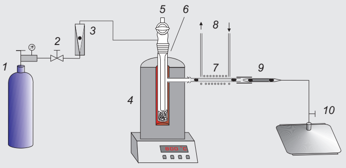


Fig. 3. *VCI combustion chamber with sampling unit*

1 synthetic air bottle with pressure controller, *2* high precision flow regulator, *3* flowmeter, *4* VCI combustion chamber with digital temperature control unit, *5* sample inlet, *6* double wall burn tube with side outlet, *7* XAD-2 adsorption tube, *8* cooling, *9* charcoal adsorption tube, *10* aluminium-coated gas sampling bag

The method contains the fire simulation, suitable sampling of effluents and chemical analysis. It allows:

- reproducible benchtop fire simulation
- qualitative and quantitative investigations of fire gases
- easy variation of parameters
- quantitative sampling of effluents

The samples are analysed post-experiment using gaschromatography coupled with mass selective, flame ionisation and thermo conductive detectors (GC-MSD, GC-FID, GC-TCD).

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*) developed by the *Verband der Chemischen Industrie e. V. (VCI)*[1]

TGA-FTIR coupling

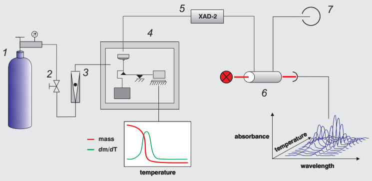

Fig. 4. *TGA-FTIR apparatus*

1 synthetic air bottle with pressure controller, *2* high precision flow regulator, *3* flowmeter, *4* TGA furnace with control unit, *5* heated transfer line with filter unit, *6* IR spektrometer equipped with heated gas cell, *7* waste

Thermal degradation studies under controlled heating rates are possible by coupling a thermogravimetric analyser with an IR spectrometer (TGA-FTIR). It is suitable for:

- determination of degradation / formation temperatures
- determination of mass loss rate
- evolved gas analysis in dependency of time/temperature
- determination of acute toxic gases (e. g. CO, HCN, HCl)
- kinetic studies

References

[1] W. Merz, H. J. Neu, M. Kuck, K. Winkler, S. Gorbach, H. Muffler; Fresenius J. Anal. Chem., *325*, **1986**, 449-460
[2] N. Sistovaris, J. Asshauer, V. Jeske, F. Schuster; Fresenius J. Anal. Chem., *334*, 3, **1989**, 221-225
[3] P. M. Lemieux, J. V. Ryan; J. Air Waste, *43*, **1993**, 1106-1115
[4] N. Büthe, Diplomarbeit, Universität Hannover, **1997**

Results

VCI fire simulation combined with GC-MSD analysis

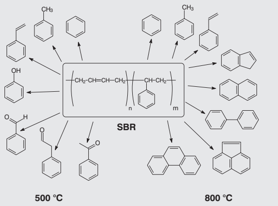

Fig. 5. *Products of incomplete combustion (PICs) of SBR*
(VCI apparatus at 500 °C and 800 °C, 25 mg SBR 1712)

The average molecular weight of the products of incomplete combustion (PICs) increases with the simulation temperature. The number of constituents of the fire effluents decreases above 800 °C.

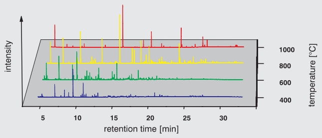

Fig. 6. *Fingerprint comparisons of PICs of SBR in dependency of simulation temperature*
(VCI apparatus, 25 mg SBR 1500, 400 mL/min air ventilation)

VCI fire simulation combined with GC-TCD analysis

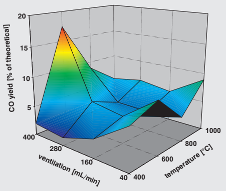

Fig. 7. *CO yields of SBR fires in dependency of temperature and ventilation*
(VCI apparatus, 25 mg SBR 1500)

The CO yields depend sensitively on the combustion parameters temperature and ventilation. The modified burn out ratio λ' increases with the simulation temperature and is determined mainly by the CO_2 yield.

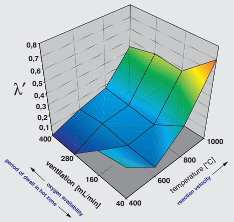

Fig. 8. *Burn out ratios λ' of SBR fires in dependency of temperature and ventilation*
(VCI apparatus, 25 mg SBR 1500)

TGA-FTIR analysis

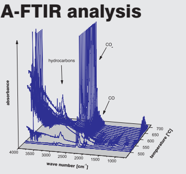

Fig. 9. *FTIR spectra in dependency of temperature*
(50 mg SBR 1500, heat rate 5 K/min)

Thermal degradation of rubber in air with increasing temperatures seems to process in two phases:

❶ chain scission and evaluation of volatile chain fragments
❷ reaction of chain fragments with oxygen, formation of CO_2/CO

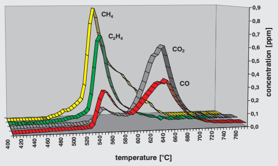

Fig. 10. *Evolved gases in dependency of temperature*
(50 mg SBR 1500, heat rate 5 K/min)

Conclusions

The qualitative composition of the fire gases depends mainly on the chemical/physical properties of the fire loads and the simulation temperatures, the quantitative composition is rather affected by the air ventilation and the dwelltime in the hot zone.

The results presented and the further research will allow the forecast of fire gas compositions and a hazard assessment of rubber fires.

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