Oxidative degradation of toluene and limonene in air by pulsed corona technology

Citation for published version (APA):

Hoeben, W. F. L. M. (2012). *Oxidative degradation of toluene and limonene in air by pulsed corona technology*. conference; PlasTEP final conference - Perspectives of Plasma Technology Symposium; 2012-12-06; 2012-12-06.

Document status and date:

Published: 01/01/2012

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Oxidative degradation of toluene and limonene in air by pulsed corona technology

W.F.L.M. Hoeben

TU/e department of Electrical Engineering

Electrical Energy Systems group, High Voltage Laboratory

P.O. Box 513

5600 MB Eindhoven

The Netherlands

TU/e

Technische Universiteit
Eindhoven
University of Technology

Where innovation starts

1. Introduction / Plasma induced degradation

Study on non-thermal plasma - induced breakdown of priority organic compounds.

Reactive Oxygen Species like e.g. $\text{OH}(X^2\Pi)$, $\text{O}(^3\text{P}, ^1\text{D}, ^1\text{S})$, $\text{O}_2(a^1\Sigma_g)$, $\text{O}_3(X^1\text{A})$ induce oxidative degradation (bond or ring cleavage, oxygen functionalization, mineralization).

Additionally excited bulk gas species like nitrogen $\text{N}_2(A^3\Sigma_u^+)$: 6.2 eV, $\text{N}_2(B)$: 7.4 eV, $\text{N}_2(a')$: 8.4 eV, UV photons (e.g. 200 nm = 6.2 eV), ions and electrons induce degradation.

1. Introduction / studied VOCs

Considered VOCs:

- Toluene $C_6H_5CH_3$:

important industrial solvent & organic synthesis building block

methylbenzene

- R(+)
Limonene $C_6H_8(CH_3)(C_3H_5)$:

odor component in waste processing facilities (citrus peels),
solvent, fragrant in cosmetics & food

(1-methyl-4-(1-methylethenyl)-cyclohexene)

1. Introduction / pulsed corona plasma

Pulsed corona discharges

- Energy efficient ROS synthesis in O_2/H_2O containing gas flows by application of steep (3 kV/ns) and short (100 ns) pulses: higher electron energies are available
- Non-thermal plasma, no bulk gas heating
- Adjustable energy density (J/L) via pulse repetition rate
- Upscalable via modular operation

The TU/e-EES prototype pulsed corona discharge system:

- 10 kW Hybrid Pulsed Power System (HPPS)
- repetition rates ($<10^3$ Hz)
- pulse energies (<10 J/p)
- reactor throughput ($<10^3$ m³/h, ε dependent)

2. Plasma generation / HPPS principles

The HPPS pulsed power system consists of:

- Resonant capacitor charger: $V_{\text{ch}} \rightarrow 30 \text{ kV}$ at $f \leq 1000 \text{ Hz}$
- Pulse forming network: switches & compresses energy in capacitor Ch to a pulse: $V_p = 60 \text{ kV}$, $I = 1.5 \text{ kA}$ (100 ns FWHM), voltage & current rise time $\sim 16 \text{ ns}$
- DC-bias network: improves matching of the pulse forming network reactor, enlarges the energy per pulse and enables electrostatic precipitation

2. Plasma generation / HPPS schematics

2. Plasma generation / HPPS photos

3. Experimental setup / reactor configuration

Reactor is vessel with 16 stainless steel cylinders, $d=160$ mm, $L=1$ m and coaxially inserted HV wire, suspended between an upper and lower frame.

Each frame is fixed to the reactor interior by four ceramic high voltage insulators. Both the pulsed power source and DC-bias are connected to the upper frame.

3. Experimental setup / diagnostics

- Cap. V-sensor, sw-Rogowski coil & Lecroy Waverunner LT584L
- Shimadzu QP2010p GC-FID-MS with SGE BP21 FFAP column
- ABB AO2000-MultiFID14 standalone flame ionization detector

3. Experimental setup / energy measurements

Pulse energy E_p [J]

$$E_p(t) = \int_{pulse} \{V_r(t) + V_{DC}(t = 0)\} \cdot I_r(t) dt$$

Energy density ε [J/L]

$$\varepsilon = \frac{f \cdot E_{p,avg}}{F}$$

Yield G [nmol/J]

$$G = \frac{10^{-6} \cdot C_0 \cdot X}{V_m \cdot \varepsilon}$$

4. Results / general observations

Oxidation of 70 ppm toluene and 10 ppm limonene at $\varepsilon=2-92$ [J/L] yields an energy density dependent complex product range.

Noxious intermediates appear (fundamental issue in advanced oxidation processes) but beyond an energy density threshold, **biocompatible carboxylic acids** like e.g. formic (HCOOH) and acetic acid (CH₃COOH) are formed.

4. Results / conversion & yield

Toluene conversion with HPPS reactor: GC-TIC data

Toluene conversion with HPPS reactor: $C_0=70$ ppm, $F=150$ m³/h, $T=25^\circ\text{C}$, $RH=57\%$

E_p (J)	f (Hz)	ε (J/L)	X (%)		G (nmol/J)
			GCMS	Integral C	
7.5	50	9	17	10	53
6.1	340	50	55	41	32
6.0	638	92	74	55	23

Limonene conversion with HPPS reactor: GC-TIC data

R(+) Limonene conversion with HPPS reactor: $C_0=10$ ppm, $F=150$ m³/h, $T=24^\circ\text{C}$, $RH=41\%$

E_p (J)	f (Hz)	ε (J/L)	X (%)		G (nmol/J)
			GCMS	Integral C	
7.5	10	2	81	67	181
7.4	60	11	100	90	38
6.4	324	50	100	96	8

4. Results / GC-TIC chromatograms

Detail GC-TIC chromatograms of toluene oxidation products at $\varepsilon=92$ J/L (right) and limonene oxidation products at $\varepsilon=2$ J/L (left) and $\varepsilon=50$ J/L (center), with identified peaks.

Peak#	Compound name
1	1-Hydroxy-2-propanone
2	Trans-p-menta-1(7),8-dien-2-ol
3	Acetic acid
4	Trans-limonene oxide
5	2-Butanone
6	4-Acetyl-1-methylcyclohexene
7	2-Acetoncyclopentanone
8	Cis-dihydrocarvone
9	3-Acetoncyclopentanone
10	3-Methylene-2,6-heptanedione
11	(E)-2-hexen-1-ol acetate
12,14	Limonene dioxide isomers
13	Trans-2-dodecen-1-ol acetate
15	Trans-2-methyl-5-(1-methylethyl)-cyclohexanone
16	Menthyl acetate

Peak#	Compound name
1	1-Hydroxy-2-propanone
2	Acetic acid
3	2-Butanone
4	1,2-Ethanediol diformate
5	Formic acid
6	4-Hydroxypentenoic acid
7	2,3-Dihydroxypropenal?
8	1-Propen-2-ol acetate
9	2,5-Hexanedione
10	(E)-2-hexen-1-ol acetate
11	Formamide
12	Trans-2-dodecen-1-ol acetate
13	2-Methoxy-1,3-dioxolane
14	Trans-2-methyl-5-(1-methylethyl)-cyclohexanone
15	2-Methyl-1,3-dioxolane

Peak #	Compound name
1	Acetic acid
2	Ethanediol diformate
3	Formic acid
4	Benzaldehyde
5	3-Methyl-2,5-furandione

5. Discussion / oxidative degradation pathways

Toluene oxidation by combined action of OH and O₂, based on C.O. Baltaretu:

5. Discussion / oxidative degradation pathways

Toluene oxidation by ozone, based on P.S. Bailey:

5. Discussion / oxidative degradation pathways

R(+) Limonene oxidation by combined action of OH and O₂, based on A. Calogirou & D. Grosjean:

5. Discussion / oxidative degradation pathways

R(+) Limonene oxidation by ozone, based on A. Calogirou & D. Grosjean:

6. Conclusions

- VOC degradation at ppm level using flows $F=150 \text{ st.m}^3/\text{h}$
 - Toluene: $C_0=70 \text{ ppm}$, $X=74\%$, $G \approx 23 \text{ nmol/J}$
products mainly acetic & formic acid
 - Limonene: $C_0=10 \text{ ppm}$, $X=81\%$ $G \approx 181 \text{ nmol/J}$
similar acids plus additional ε -dependent oxygenates
- High conversion at low energy densities may need attention!
- FFAP GC column is very suitable for resolving complex oxidation product mixtures
- The integral carbon FID analyzer is a robust detector for determination of lower limit hydrocarbon conversion levels, when a GC-MS is no option

Reference

W.F.L.M. Hoeben, F.J.C.M. Beckers, A.J.M. Pemen,
E.J.M. van Heesch and W.L. Kling
2012 *J. Phys. D: Appl. Phys.* **45** 055202
[doi:10.1088/0022-3727/45/5/055202](https://doi.org/10.1088/0022-3727/45/5/055202)
and references therein

Thank you for your interest!