Pyrolysis experiments to assess cigarette paper design contribution to thermal degradation without and with tobacco

DURÓT N[1]., OUAR Z[1]., RAVERDY LAMBERT D[1]., HERVE R[2]

[1]SWM INTL c/o LTR Industries, Usine Le Mans, Allonnes Cedex 72702 France
[2]SWM INTL c/o PDM industries, Kerisole, Quimperlé, France

Content

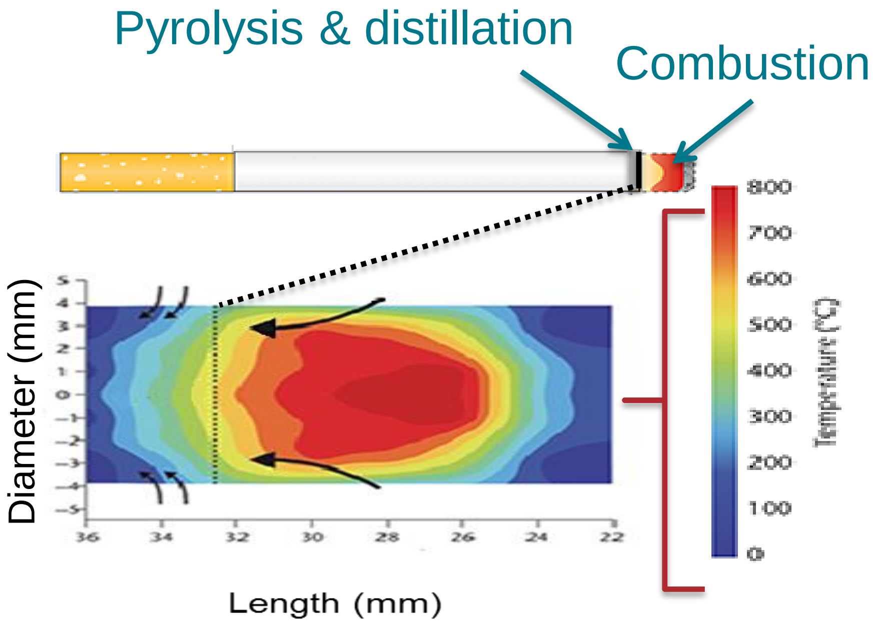
1.Context & objectives

Emerging regulations on tobacco products & ingredients : pyrolysis is one of the candidate tool to assess design modification

- ☐ Compare thermal degradation components of cigarette paper vs cellulose
- ☐ Evaluate the effects of the cigarette paper design alone and combined to a tobacco matrix on thermal degradation components

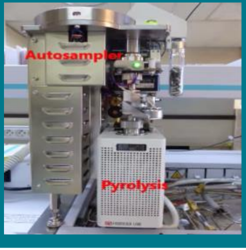
2. Pyrolysis GC/MS conditions definition

Temperature range in a burning cigarette



Temperature range °C	Phenomena
250 -300	Decomposition of citrates cellulose depolymerization, hemicellulose decomposition
300-425	Cellulose decomposition
425-625	Char decomposition
625-900	$CaCO_3$ decomposition

2. Pyrolysis GC/MS conditions

Multi-shot pyrolyzer **EGA/PY3030D** **Shimadzu** 	**Heating rate**	**Temperature °C**	**% O_2 in nitrogen**
	Isothermal Duration 0.1 min	350, 450, 500, 600, 700, 800, 900,1000	2, 9, 20

GC/MS **QP2010** **Ultra NCI** **Shimadzu**	**Column**	**GC parameters**	**Electron impact MS parameters**
	Column HP-5MS Length 30m Film thickness 0,25µm Diameter 0,25mm	**T_{oven} =** 90 isotherm and gradient up to 270 °C **$T_{Injector}$ =** 250°C **Splitless mode** **Carrier gas :** He	$T_{Ion\ source}$ = 230°C $T_{Interface}$ = 250°C Components identification with NIST base & integration on the main ion

Analyses	**4 replicates per sample & condition (mean, IC95% , COV on main components)**

2. Pyrolysis GC/MS conditions
Oxygen level effect

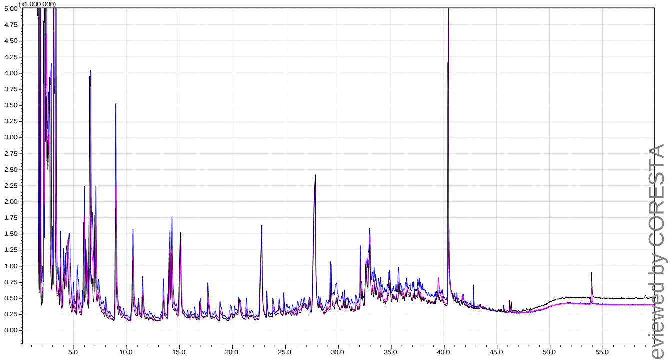
With the different oxygen levels (2% - 9% - 20%):

same components are recovered but their intensity vary

9 vs 2% O_2 : reduction of some ketons, ethylene glycol

At 20% O_2 :

- larger reduction for certains ketons, propylene oxide, heptanal, glucopyranose derivatives
- increase of dihydrofuran & pentanedione

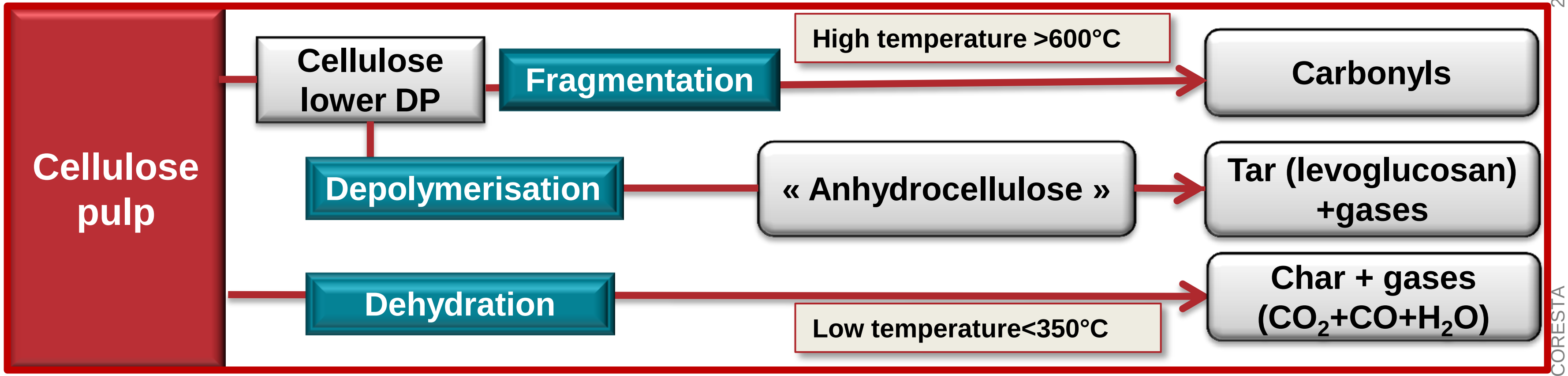


eg: Total Ion chromatograms of cigarette paper pyrolysis at 450°C

Higher O_2 concentration
- **Accelerates cellulose degradation**
- **Catalyzes thermal degradation of solid char & $CaCO_3$**

3.Cigarette vs cellulose paper comparison Thermal degradation of ingredients

Cigarette paper ingredients



Cellulose pulp

Cellulose lower DP

Fragmentation

High temperature >600°C

Carbonyls

Depolymerisation

« Anhydrocellulose »

Tar (levoglucosan) +gases

Dehydration

Low temperature<350°C

Char + gases (CO_2+CO+H_2O)

Filler $CaCO_3$

Calcite $\xrightarrow{600\text{ -}900°C}$ CaO +CO_2

Burning salt Citrate Na/K

$C_6H_5O_7Na_3 \xrightarrow{250°C} Na_2CO_3$

$C_6H_5O_7K_3 \xrightarrow{230°C} K_2CO_3$

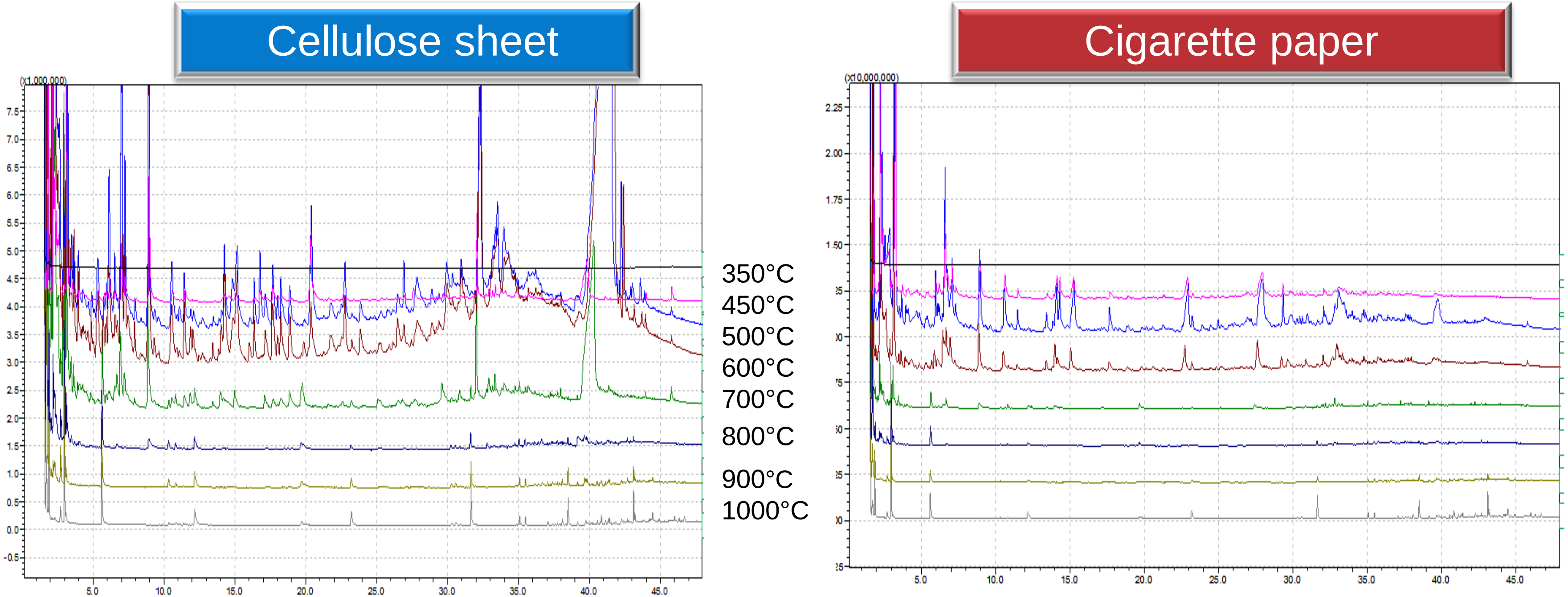
3.Cigarette vs cellulose paper comparison
Sampling and pyrolysis conditions

	Cellulose sheet	Cigarette paper	
Sampling	Cellulose pulp	Cellulose pulp +$CaCO_3$ 35% +citrate K 1,5%	Isofiber weight 20 g/m²

	Heading rate & duration	Temperature	% O_2 in nitrogen
Pyrolysis conditions	Isothermal 0.1 min	350, 450, 500, 600, 700, 800, 900, 1000	9%

- **4 replicates per sample & per condition**

3.Cigarette vs cellulose paper comparison Thermal degradation profiles

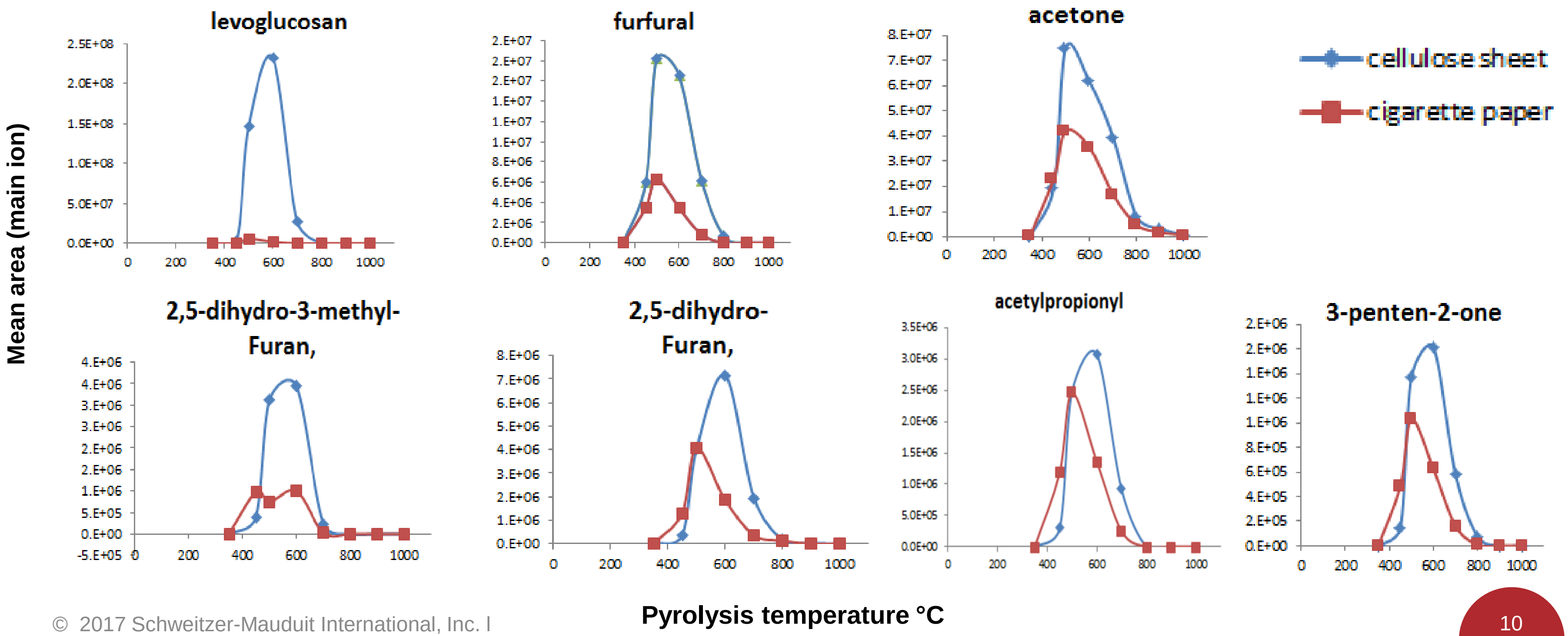


Pyrolysis total ion chromatograms

- Limited number of thermal degradation products at 350°C
- Strong variations between cellulose and cig paper in the range 450-700°C

3.Cigarette vs cellulose paper comparison Thermal degradation components

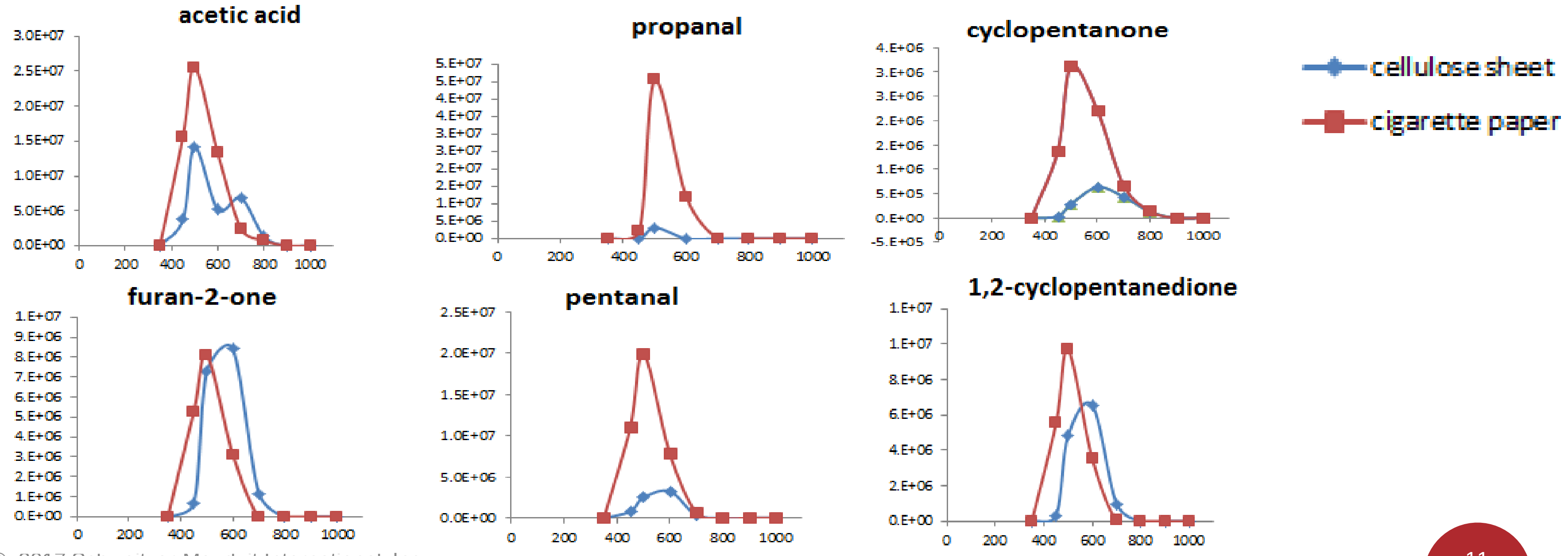
Cellulose sheet : higher amounts of levoglucosan & furfural , furan derivatives and ketons



3.Cigarette vs cellulose paper comparison
Thermal degradation components

Cigarette paper :

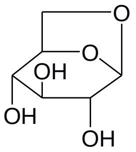
- Higher amounts of acids, propanal, pentanal & cyclopentanone derivatives
- Release seems to start at lower temperature for certain analytes



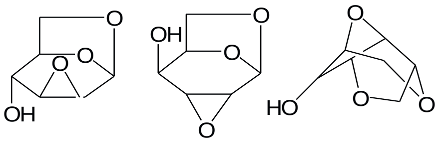
3.Cigarette vs cellulose paper comparison Thermal degradation : main conclusions

Cellulose sheet ≠ **Cigarette paper**

mainly depolymerization & fragmentation

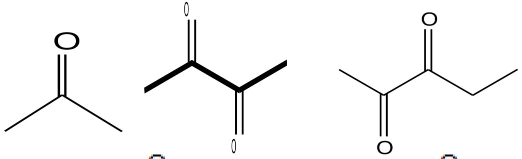


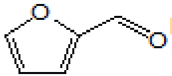
Levoglucosan



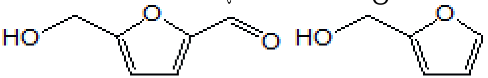
Anhydrosugars

Carbonyls

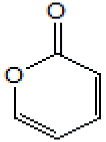




Furfural

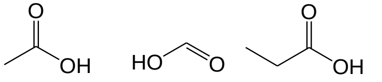


Furan derivatives



Pyranone derivatives

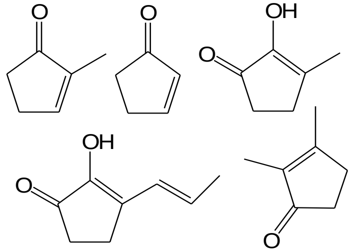
mainly dehydration (combustion salt)

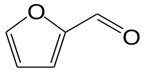


Acetic, formic, propanoic acid

Char

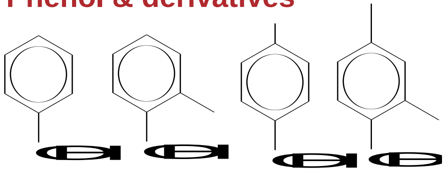
Cyclopentenones





Furfural

Phenol & derivatives



4.Cigarette paper design effect DOE parameters

- **Level & type of ingredients**
  - Filler
  - Citrate K, Na/K
- **Cig paper parameters**
  - Permeability
  - Basis weight

Draper Lin face centered matrix	Permeability (CU)	Basis weight (g/m²)	Citrate (%)	K ratio for citrate	Filler (g/m²)
Min	50	26	0.8	0.33	8.78
Center	65	29	1.4	0.66	9.28
Max	80	32	2	1	9.78

4.Cigarette paper design effect
Sampling & experimental conditions

Sampling

Cig Paper matrix

Cigarette paper sample ≅1 mg

Tobacco blend

Flue-cured tobacco blend

Blend 50 cig

Cig paper+ tobacco matrix[1]

Paper 6% 0,16-0,20mg

Tob. 94% 2,50±0,05mg

[1]: *paper / tobacco ratio representative of a king size cigarette*

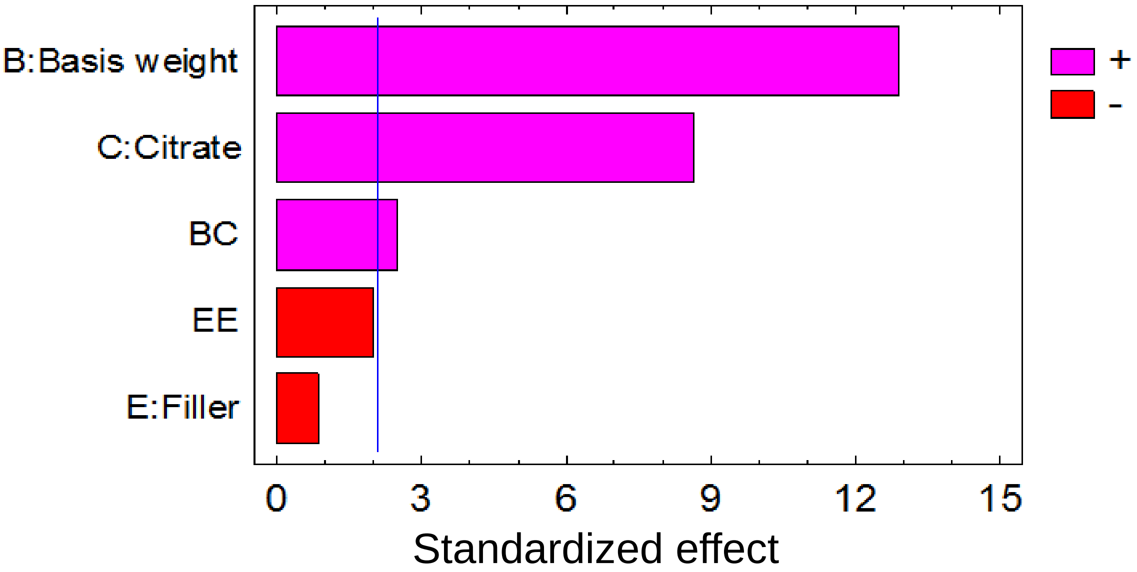
	Heating rate & duration	temperature °C	%O2 in nitrogen
Pyrolysis conditions	Isothermal 0.1 min	450 700	9%

- ➢ **4 replicates per sample & per condition**

4.Cigarette paper design effect
Statistical analysis

DOE results: cigarette paper pyrolysis at 450°C

Standardized Pareto chart for acetic acid



Model validation
$R^2>90\%$

Significant effect if
P value < 0,05

$R^2=92,2\%$

4.Cigarette paper design effect
Pyrolysis results

Cigarette paper design pyrolysis 450°C

Basis weight significant effect on carbonyls, additional effect of citrate except for acetone & furfural

	Permeability	Basis Weight	Citrate	K ratio	Filler	1st order interactions	2nd Order interactions	R^2
Acetone		↗					K^2	72
Diacetyl		↗	↗				P^2	**93**
Cyclopentenone		↗	↗				P^2	**93**
Acetylpropionyl		↗	↗			BW x Citrate		**92**
Furfural		↗						87
Acetic acid		↗	↗			BW x Citrate		**92**
1,3-Cyclopentadiene		↗	↗			BW x Citrate	C^2	**90**
2,5-Dihydrofuran		↗	↗					87
Furanmethanol		↗						**91**

4.Cigarette paper design effect
Pyrolysis results

Cigarette paper design pyrolysis 700°C

Significant effects

- basis weight, filler and citrate level for carbonyls, K ratio in addition for crotonaldehyde
- basis weight for phenol

		Permeability	Basis Weight	Citrate	K ratio	Filler	1st order interactions	2ndOrder interactions	R^2
Carbonyls	**Crotonaldehyde**		↗		↘	↘			**94**
	Benzaldehyde		↗	↗		↘		**K^2**	**95**
	3-methyl cyclopenten-1-one		↗	↗		↘		K^2	96
	Butyrolactone		↗	↗		↘		K^2	96
	Hydroxy-2-butanone		↗	↗	↗	↘			96
Phenol & derivatives	**Phenol**		↗						**92**
	Methyl phenols		↗			↘			>93
	Dimethyl phenols		↗	↗		↘			>95

4.Cigarette paper design effect
Pyrolysis results

Cigarette paper design pyrolysis 700°C

- Significant effects of basis weight for aromatics, PAH, and benzofuran
- Some significant effects of filler level and 2nd order interactions K ratio, citrate level

		Permeability	Basis Weight	Citrate	K ratio	Filler	1st order interactions	2nd order interactions	R^2
Aromatics	**Benzene**		↗			↘		K^2	**93**
	Xylene		↗			↘		K^2	**96**
	Toluene		↗			↘		K^2 C^2	**96**
	Styrene		↗					K^2	**93**
PAH	**Naphtalene**		↗					K^2	**91**
	Anthracene		↗			↘			**90**
	Fluorene		↗			↘			**93**
	Biphenyl		↗						**92**
	Cyclopentadiene		↗			↘		K^2	96
	Benzofuran		↗					K^2	94

4.Cigarette paper design effect
Pyrolysis results in a tobacco matrix

Cigarette paper* + tobacco matrix vs tobacco matrix : pyrolysis profiles

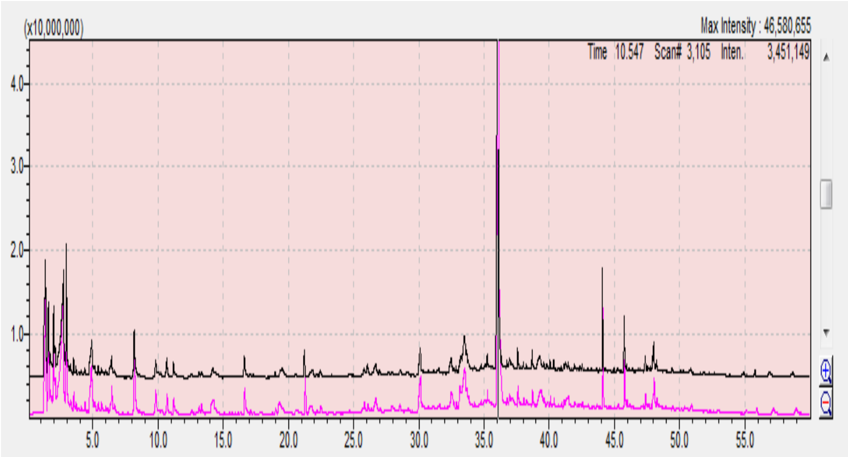
- Similar chromatogram profile for a ratio 94 % tobacco-6% cigarette paper
- No additional components identified

— Tobacco matrix chromatogram

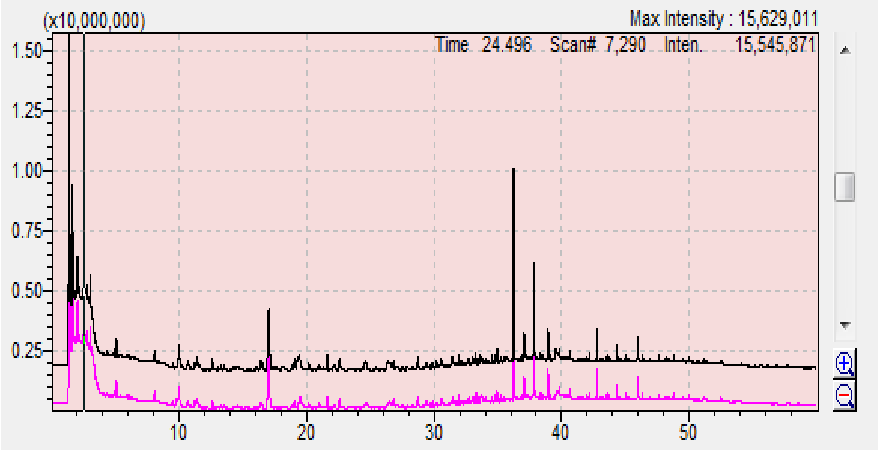
— Cigarette paper+tobacco matrix chromatogram

450°C

Total ion area



700°C



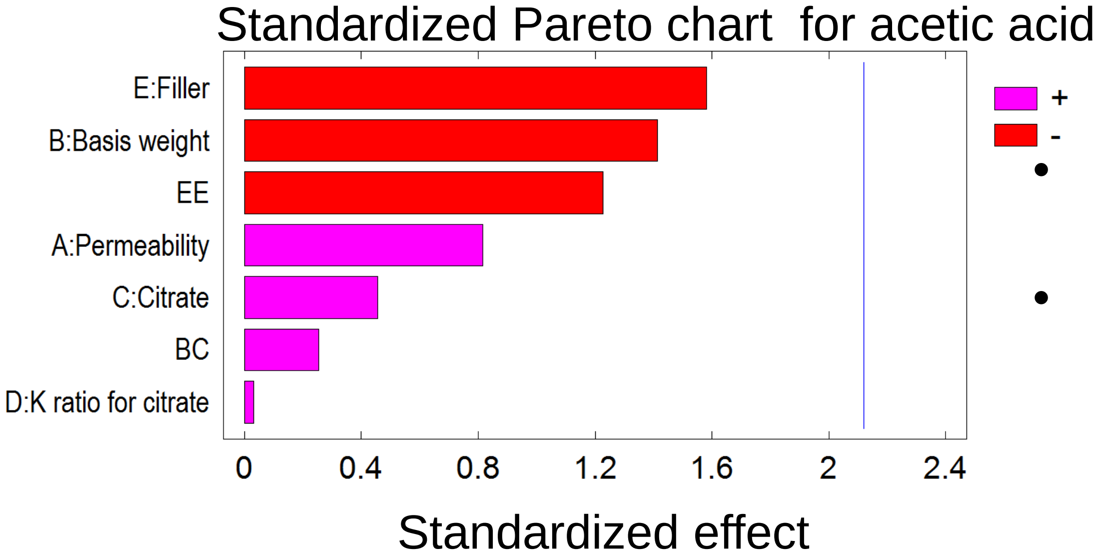
* Central point of cigarette design DOE

4.Cigarette paper design effect
Pyrolysis results in a tobacco matrix

Cigarette paper design in tobacco matrix pyrolysis at 450°C

Harmful components generated at 450°C

- No significant effect of cigarette paper design in a tobacco matrix



- P value > 0,05
  => effects are not significant
- R² < 60%
  => models are not validated

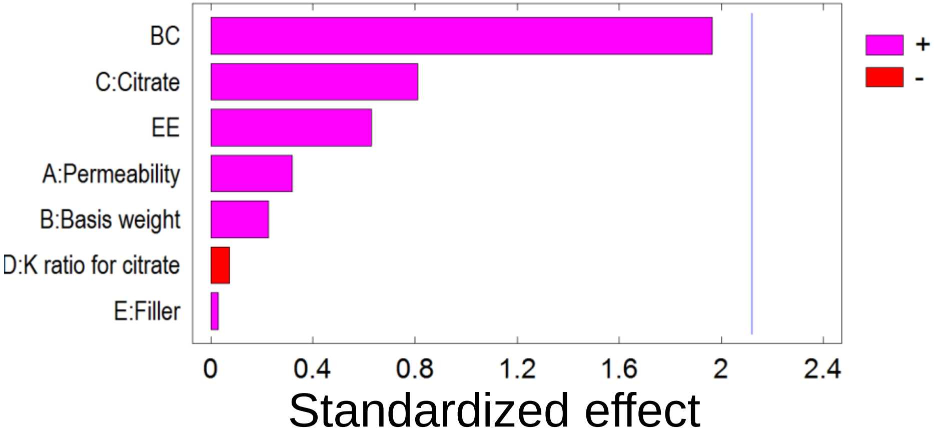
4.Cigarette paper design effect
Pyrolysis results in a tobacco matrix

Cigarette paper design in tobacco matrix pyrolysis at 700°C

Harmful components generated at 700°C :

- No significant effect of cigarette paper design in a tobacco matrix
- Low contribution of cigarette paper design when evaluated in a tobacco matrix

Standardized Pareto chart for toluene



- P value > 0,05

  => effects are not significant
- R² < 60%

  => models are not validated

5.Conclusions

- Pyrolysis experiments are useful & complementary tool to identify harmful by-products components generated by thermal degradation of ingredients in a matrix

- Help to identify the level of the effect of each ingredient and its potential interaction with paper or tobacco

5.Conclusions

- Thermal degradation profiles: cigarette paper ≠ cellulose

  => harmful components generated by cigarette paper pyrolysis can not be extrapoled or predicted from experiments on cellulose alone

- Basis weight, filler and citrate levels changes affect the amount of certain harmful components generated such as carbonyls, volatiles & PAH when cigarette paper is evaluated alone

- These effects are not significant when cigarette paper is evaluated with a tobacco matrix mocking the paper/tobacco ratio of a king size cigarette

Thank you for your attention