On the significance of methyl chloride in gasification processes

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ON THE SIGNIFICANCE OF METHYL CHLORIDE IN GASIFICATION PROCESSES

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Summary

I An analytical procedure for methyl chloride in producer gas has been developed.

II The method has been applied to producer gasses from both updraft and LT-CFB gasifiers.

III Consequences for the end-use and aspects of possible up-grading of the gas has been identified.

$$CH_3\text{-}Cl$$

Layout of presentation

Discovering the significance of *methyl chloride*

Analytical strategies

Results

How is *methyl chloride* formed ?

Consequences of the presence of *methyl chloride*

Chlorine in Bio-energy

The role of chlorine in gasification/combustion is general classified as an inorganic aspect associated with the formation of deposits or ash quality.

The role of simple chlorinated organic compounds is rarely discussed.

Chlorine in producer gas

Gas engines were fuelled by highly purified producer gas.

However, large quantities of chlorine was accumulated in the lubricating oils.

The accumulation was significant, i.e. amounting to 1-2 ppm Cl/hour.

Very low pH and high chloride concentration in the exhaust gas condensate

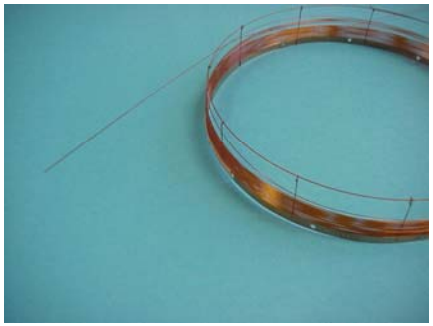
Chlorine in the Bio-sphere

Methyl chloride is the most abundant organic chlorine compound in the atmosphere contributing to 16 % of the organic chlorine in the troposphere.

Volatilization of chloride as methyl chloride may occur during biomass burning, e.g. smoldering savannah fires.

These emissions have been estimated to 1 Tg pr year on global scale.

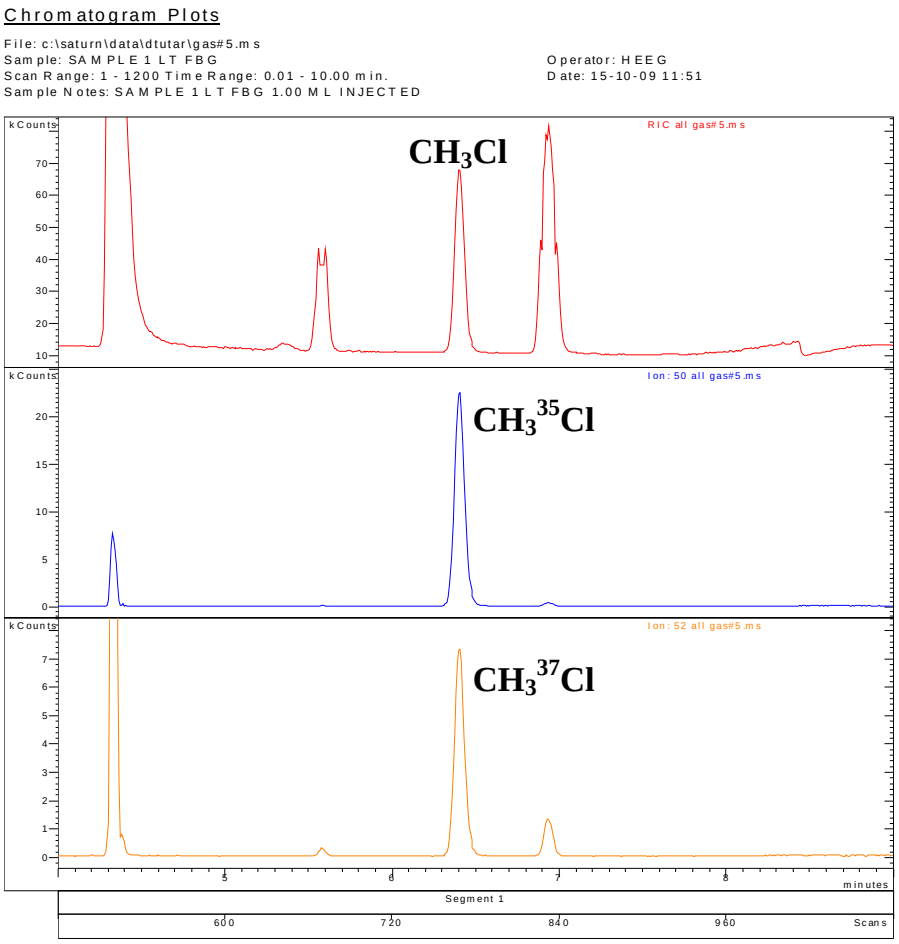
Analytical methods



Gas chromatography / mass spectrometry in combination with, e.g. pyrolytical techniques.

Analytical performance

Determination of MeCl in producer gas (LT-CFB)

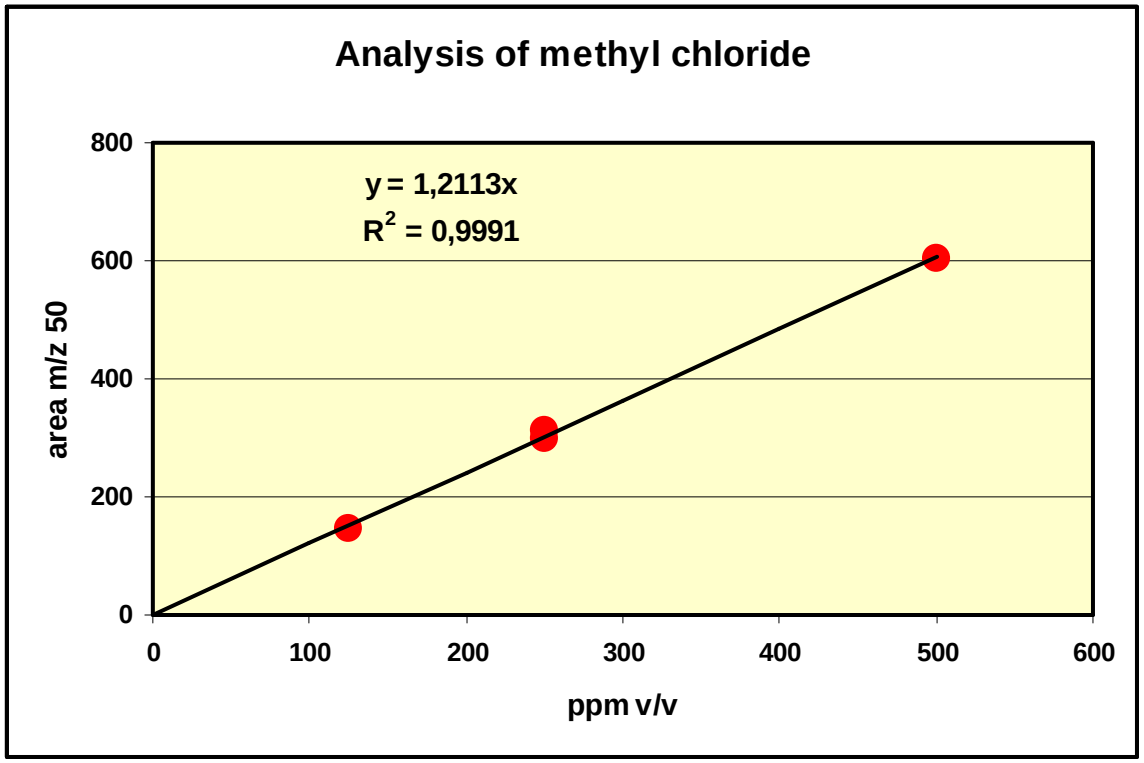


Isotopic signature

$I(Me^{37}Cl)/I(Me^{35}Cl)$

Citrus shells: 0.347
Auth. MeCl: 0.330
Cl (lit.value): 0.320

Quantitative determination of MeCl



Methyl chloride (99.8%) Gerling Holz (Germany).
Methyl chloride has bp -24.2 ºC and mp -97 ºC.

Quantitative determination of MeCl

Gasifier technology	Fuel	Chlorine	n	MeCl, ppm v/v
Up-draft	Wood chips	$12^{a}/54^{b}$ ppm	2	30
LT-CFB	Citrus shell fibers	0.061 %	3	40 - 200
LT-CFB	Wheat straw	0.24 %	3	120 - 200

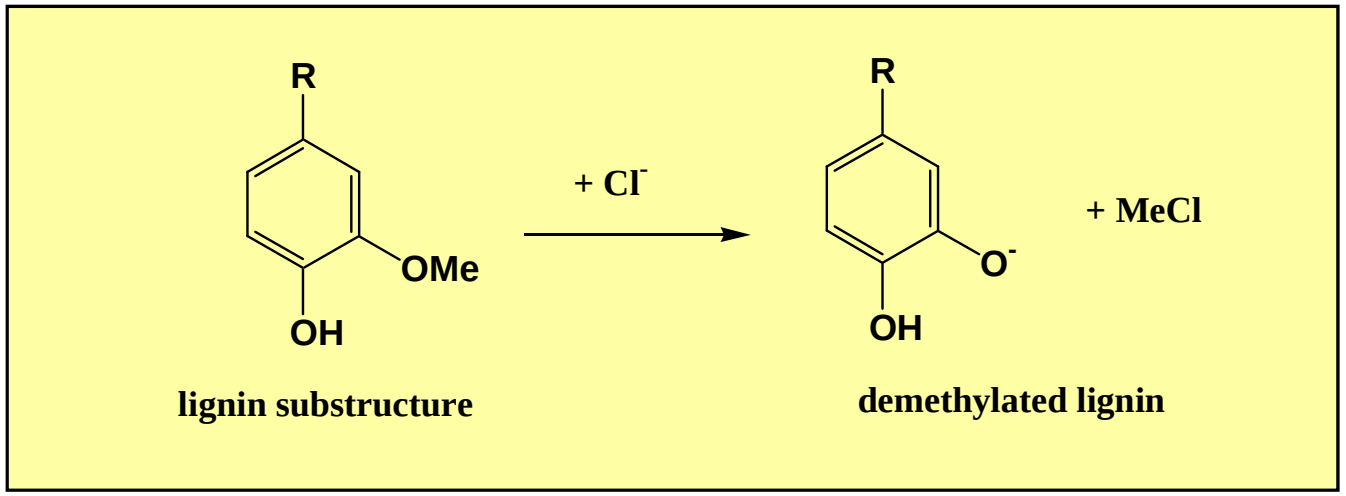
Methyl chloride concentration in various producer gases

[a]wood chips, [b]green wood chips.

n is the number of independent determinations.

The origin of MeCl – high temperature process

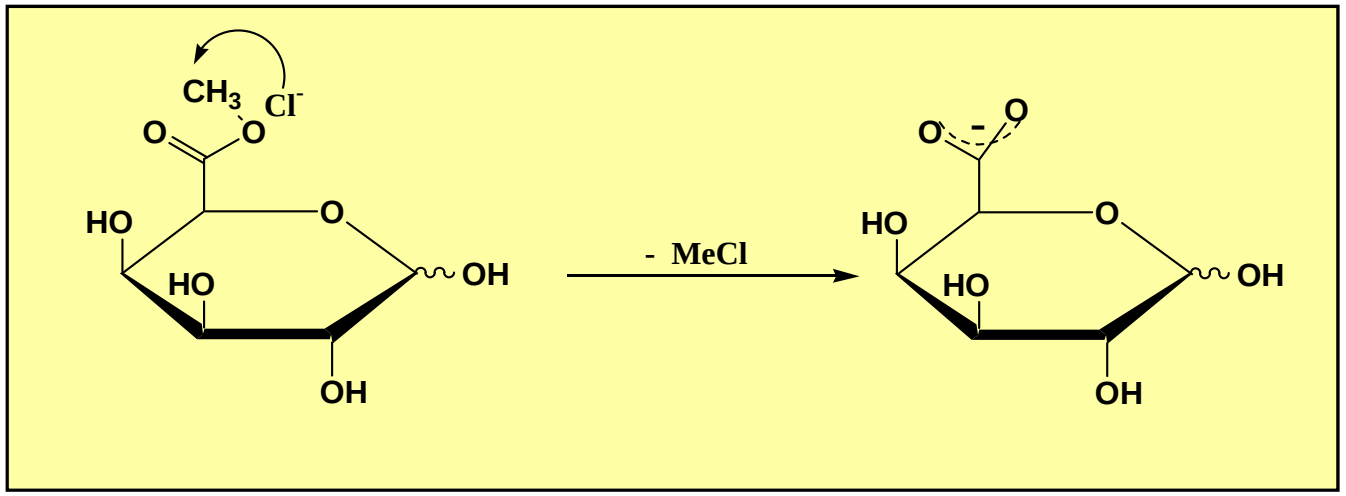
The possible reaction involving lignin was investigated by heating lignin with approximately 1 % KCl.
The reaction revealed a maximum at 600 – 800 °C.



Semi-quantitative analyses suggested this contribution to be a minor route, e.g. a few pct. in biomass.

The origin of MeCl –low temperature process

Formation of methyl chloride may occur from the wide-spread plant component pectin.



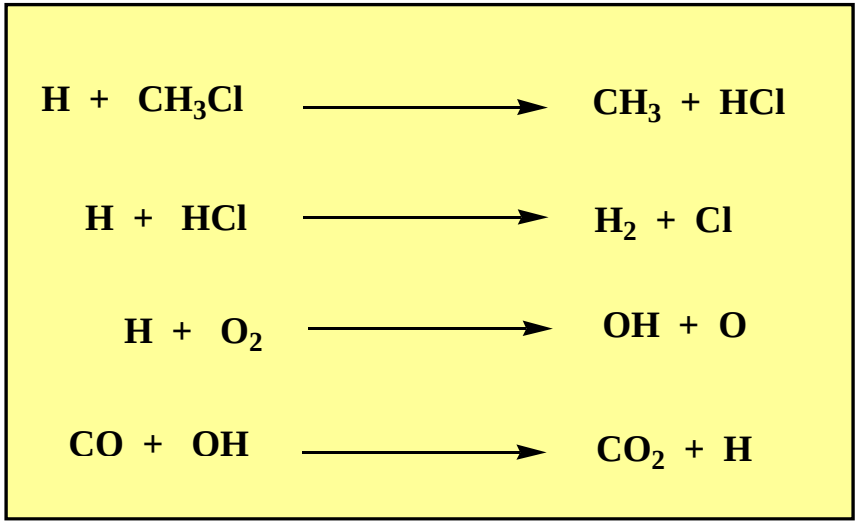
Science
AAAS

Chloride Methylation by Plant Pectin: An Efficient Environmentally Significant Process
John T. G. Hamilton, *et al.*
Science **301**, 206 (2003);
DOI: 10.1126/science.1085036

Combustion of MeCl

The complete oxidation of MeCl leads to water, carbon dioxide and hydrogen chloride.

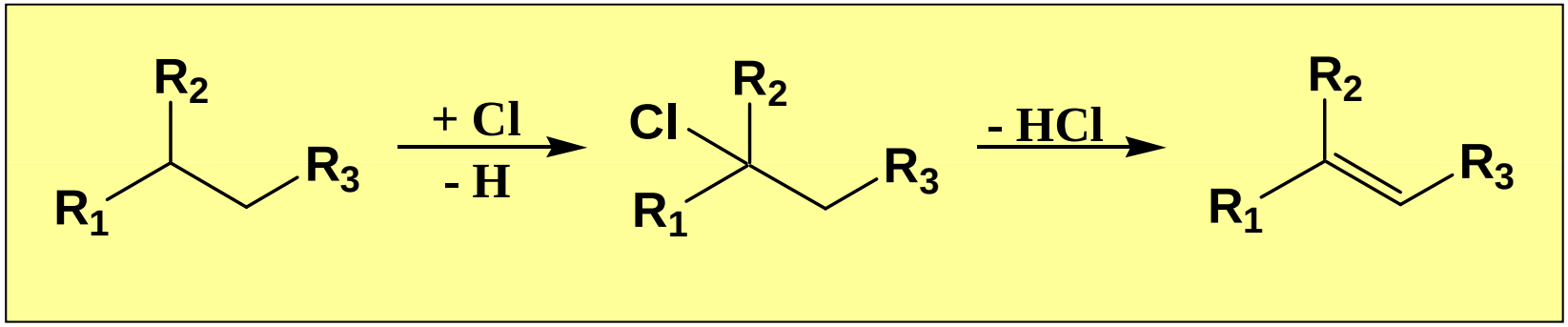
Co-combustion of MeCl will normally give a faster initial step followed by a reduced rate of the combustion propagation.



S.L.Hung and L.D. Pfefferie;
Environ. Sci. Tech. 23 (1989) p.1085.

Combustion of MeCl

In the case that the producer gas is to be used on gas engines the intermediacy of chlorine atoms in the combustion process may lead to accumulation of covalently bound chlorine in the lubricating oil.



Reduction of MeCl concentrations in producer gas

These attempts naturally fall in two distinc groups namely:

1) **attempts to remove selectively methyl chloride**
   The methods have all some drawbacks. i.e. in reducing energy efficiency caused by thermal cycles or otherwise introducing significant cost to the process.

2) **attempts to avoid the generation of methyl chloride**
   Thermal pre-treatment may advantageously be carried out in connection with a torrefaction based upgrading of the biomass. Hydrolysis of the pectin is an other option.

Conclusion

- ✓ **An analytical method for methyl chloride in producer gas has been developed.**
- ✓ **Producer gasses from updraft and LT-CFB gasifiers fuelled with different feed stocks have been analyzed.**
- ✓ **Consequences for the end-use of the produced gas and aspects of possible reduction methods have been identified.**
- ✓ **Pre-treatment of the fuel appears realistic.**