

CTC Production and Consumption

1. Routes to produce CTC
 - chloromethanes
 - perchloroethylene/CTC
 - deliberate via carbon disulphide

2. Consumption Patterns of CTC
 - chemical intermediate
 - process agent/ lab

3. Emissions of CTC
 - fugitive from production and use

4. Summary

5. Blue Sky
 - Some ideas on the mystery

CTC Production and Consumption: Chloromethanes

- In >90% of cases chloromethanes are made by reacting methyl chloride with chlorine: coproduction of methylene chloride, chloroform and CTC is inevitable by any route
- *If CTC is minimised, yield ratios to CTC would be +/- 4-5% on all chloromethanes or +/- 7% on chloroform*
- Some producers have higher ratios and some produce CTC deliberately for intermediate
- *Global capacity for chloromethanes is 3785 ktpa (35 plants): equal to 189.3 kt of CTC at capacity at 5% CTC*
- Global production chloromethanes 2014 was 2785 kt: estimated CTC output was 163.7 kt

CTC Production and Consumption: Chloromethanes

- Production \neq Emissions!
- Disposition is to
 - Chemical intermediate (HFC/PCE...)
 - Process agent and lab use
 - Distillation of “crude” may be needed= tars
 - Incineration on/offsite
 - Some inevitable fugitives

CTC Production and Consumption: Chloromethanes Putting numbers on it (kilotons/2014)

Region	Plants	Capacity CM	Actual CM	Actual CTC 5%
Europe	6	660	500	29.5
Russia	2	80	60	2.7
NAFTA	3	420	380	25.0
China	16	2150	1450	76.5
India	4	210	195	20.0
Japan	3	185	140	7.0
S Korea	1	80	60	3.0
TOTAL	35	3785	2785	163.7

Sources and verifications: NSA database, DG Clima, US-EPA, UN Comtrade, Industry, UNMLF, WB-FECO, TEAP

CTC Production and Consumption: PCE and CTC (2014)

- PCE/CTC plants pyrolyse waste chlorocarbons in the presence of chlorine: create PCE and CTC in differing ratios and HCl. Revalorisation issue (add value to waste). Hexa-tars incinerated.
- *Mainly made for CFC boom: bias to CTC, some PCE to CFC113, some to solvent. CTC was once >1 million tpa.*
- Mainly modified, with investment, to 100% PCE cycle. Can consume crude CTC from chloromethanes.(but can make each)
- *Global capacity for PCE/CTC is 360 ktpa (5 plants): equal to 0% of CTC. Deliberate production PCE 300 kt, Deliberate CTC 39 kt*

CTC Production and Consumption: PCE/CTC

- Production \neq Emissions!
- Disposition is to
 - Chemical intermediate (HFC/PCE...)
 - Process agent and lab use
 - Such plants clean-up crude CTC
 - Incineration of wastes onsite
 - Some inevitable fugitives

CTC Production and Consumption: PCE/CTC Putting numbers on it (kilotons/2014)

Region	Plants	Capacity PCE/ CTC	CTC	Actual PCE/ CTC	Actual CTC
Europe	3	195.0	0-100%	160.0	9.0
Russia	0	0	0	0	0
NAFTA	2	135.0	0-100%	113.0	30.0
China	2	30.0	Makes PCE from CM CTC	27.0	0
India	0	0	0	0	0
Japan	0	0	0	0	0
S Korea	0	0	0	0	0
TOTAL	5	360(+)	0	300	39

Sources and verifications: NSA database, DG Clima, US-EPA, UN Comtrade, Industry, UNMLF, WB-FECO, TEAP

CTC Production and Consumption: CMs and PCE/CTC Totalling CTC(metric tons/2014)

Region	CTC from CM	CTC from PCE/CTC	Actual CTC
Europe	29.5	9.0	38.5
Russia	2.7	0	2.7
NAFTA	25	30	55.0
China	76.5	0	76.5
India	210	0	20.0
Japan	7	0	7.0
S Korea	3.0	0	3.0
TOTAL	163.7	39.0	202.7

Sources and verifications: NSA database, DG Clima, US-EPA, UN Comtrade, Industry, UNMLF, WB-FECO, TEAP

CTC Production and Consumption: All sources Where is it used?(kilotons/2014)

Region	PCE/CTC	CTC/HFC	CTC/DVAC	CTC/MeC and other	CTC Incineration	P Agent/lab	TOTAL
Europe	16.0	7.0	0	0	15.0	0.5	38.5
Russia	0	0	0	0	2.2	0.5	2.7
NAFTA	21.5	30.5	0	0	1.5	1.5	55.0
China	27.0	20.0	3.0	26.0	0	0.1	76.1
India	0	0	20.0	0	0	0	20.0
Japan	0	0	0	0	7.0	0	7.0
S Korea	0	0	0	0	3.0	0	3.0
TOTAL	64.5	57.5	23	26	28.7	2.6	202.3

Sources and verifications: NSA database, DG Clima, US-EPA, UN Comtrade, Industry, UNMLF, WB-FECO, TEAP

CTC Production and Consumption:

- Kharasch reactions are vital to CTC intermediate use
- $\text{CH}_2=\text{CH}_2 + \text{CTC} = \text{CCl}_3\text{-CH}_2\text{-CH}_2\text{Cl}$ (starter to HFO1234yf)
- $\text{CH}_2=\text{CHCl} + \text{CTC} = \text{CCl}_3\text{-CH}_2\text{-CHCl}_2$ (starter for HFC245fa, HCFO1233xd, HFO1234ze)
- $\text{CH}_2=\text{CH-CN}_3 + \text{CTC} = \text{tetrachlorobutyronitrile}$ (starter to DVAC synthetic pyrethroid)
- And... $\text{CTC} + 2\text{Cl}_2 + \text{CH}_4 = \text{CCl}_2=\text{CCl}_2$ (PCE + 4HCl)

CTC Production and Consumption: All sources Likely emissions/fugitives(kilotons/2014)

Region	From PCE/CTC	From CTC/HFC	From CTC/ DVAC	From CTC/MeC and other	From CTC Incineration	From P Agent/lab	From CM plants at 0.4%	TOTAL
Europe	0	0	0	0	0	0.01	2.01	2.02
Russia	0	0	0	0	0	0.20	0.44	0.64
NAFTA	0	0	0	0	0	0.04	1.56	1.60
China	0.2	0.2	0.1	0.2	0	0.05	6.55	7.30
India	0	0	1.0	0	0	0	1.78	2.78
Japan	0	0	0	0	0	0	0.56	0.56
S Korea	0	0	0	0	0	0	0.24	0.24
TOTAL	0.2	0.2	1.1	0.2	0	0.3	13.14	15.14

Sources and verifications: NSA database, DG Clima, US-EPA, UN Comtrade, Industry, UNMLF, WB-FECO, TEAP

CTC Production, Consumption and Emissions

- Based on an industry perspective, which has been verified extensively with agencies and producers, a calculation of just over 15 kt emissive in 2014 is not close enough to top-down calculations to be a gap-solver.
- What else is there?
 - Obabashi et al paper (2007) shows household bleach (NaOCl) with added surfactants can have up to 10% of CTC in the “headspace”. Not verified by this reviewer but such bleaches have large markets (30 million tons in 2013) and in addition in N America are frequently added to top-load washing machines.
 - WASTE!

CTC Production, Consumption and Emissions- WASTE

- This is an analysis of an oxy-EDC stream from the late 1900s
- Oxy EDC and direct chlorination EDC are combined and reacted to make VCM and in turn PVC
- Oxy-EDC generates about 0.6% waste stream: it is produced at >50% of all EDC which is today 60 million tons. Direct EDC is \pm 0.1% waste.
- It is mostly incinerated but has found its way historically into aqueous media and gaseous vents as well as soil

Substance	Amount (Weight %)
1,2-Dichloroethane (EDC)	25.8
CTC	21.9
Chloroform	19.8
1,1 Dichloroethane	6.1
Monochlorobutadienes	6.0
Trichloroethylene	5.1
Cis-1,2-dichloroethylene	4.4
Vinylidene chloride (1,1-DCE)	3.9
Trans-1,2- dichloroethylene	3.6
Vinyl chloride	0.4
Benzene	0.4
Methylene chloride	0.3
Unknown	2.3
Total	100

CTC Production, Consumption and Emissions- WASTE

- The maths say 79 kt (2014) but remember production \neq emission. Vast majority is captured by incineration or in-line thermal oxidisers.
-BUT not always historically

CTC Production and Consumption

Thank you for your kind attention!