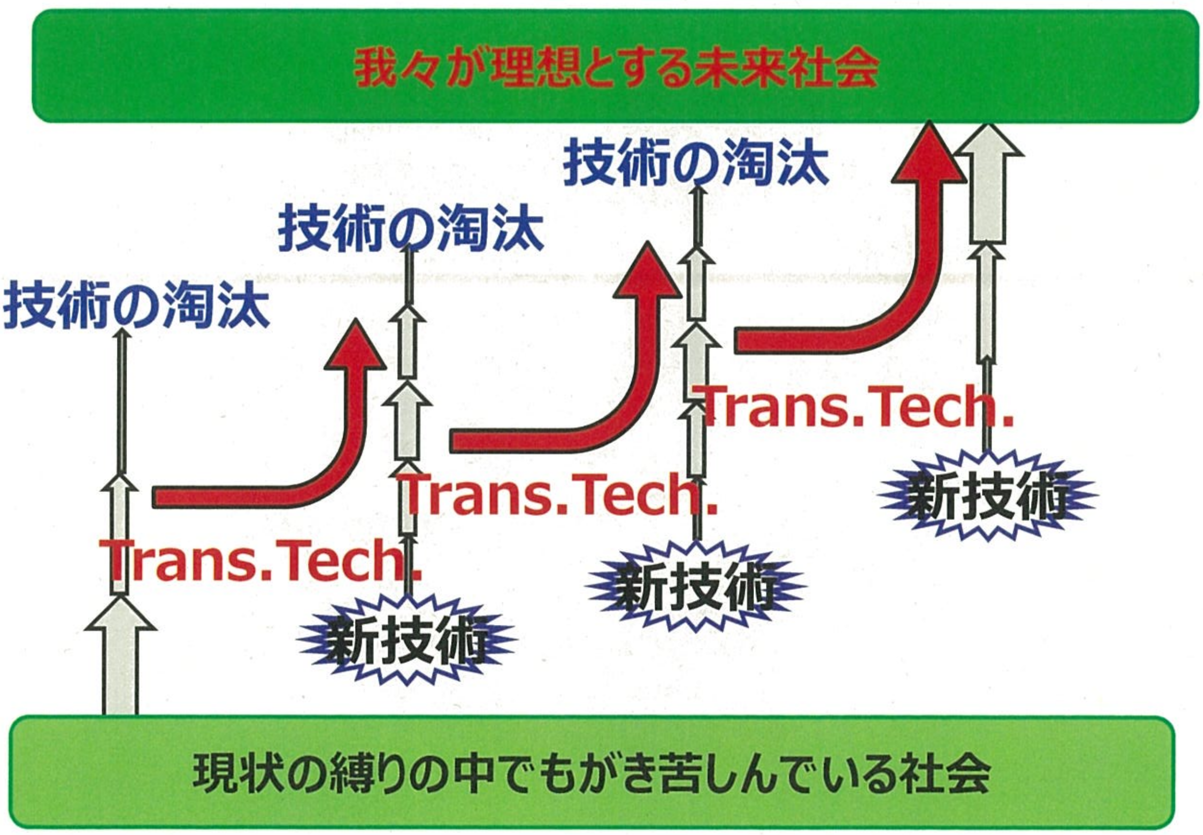
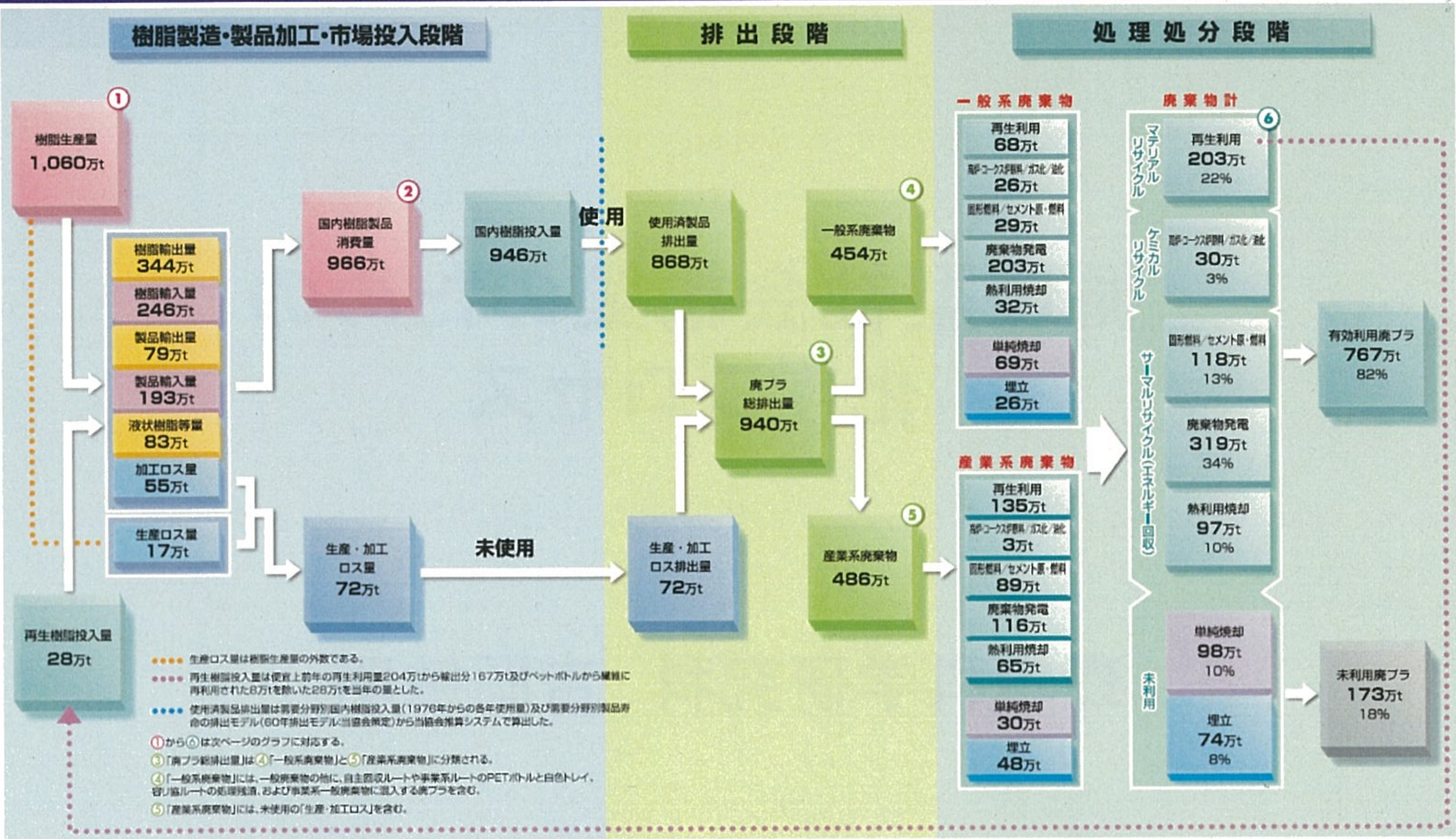
循環型社会構築のための化学プロセス

環境科学研究科　吉岡敏明

Transfer Technology (TransTech)



プラスチックのマテリアルフロー（2013）



出典：プラスチック循環利用協会（2014）

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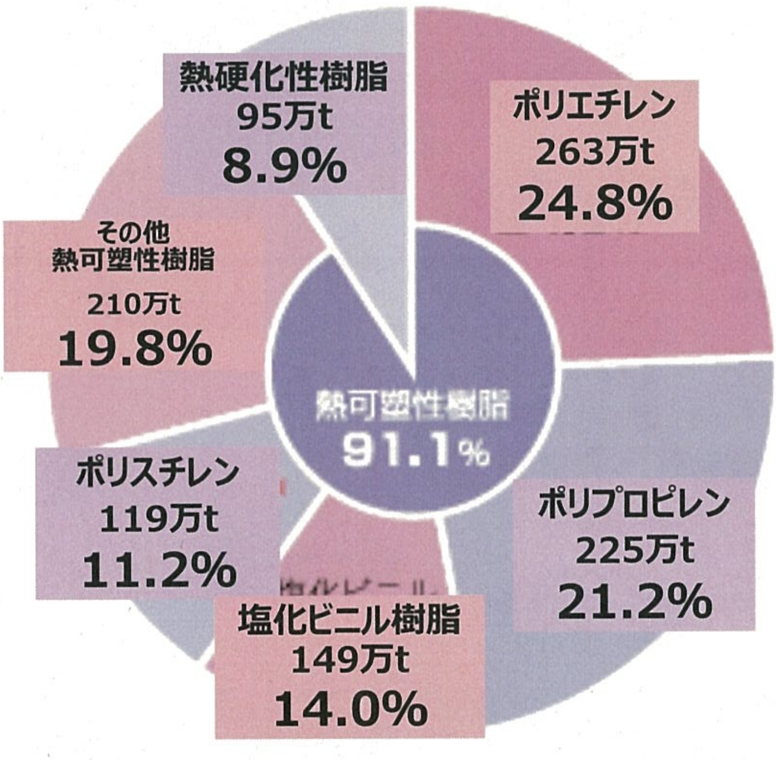
プラスチック樹脂生産の内訳（2013）



出典：プラスチック循環利用協会（2014）

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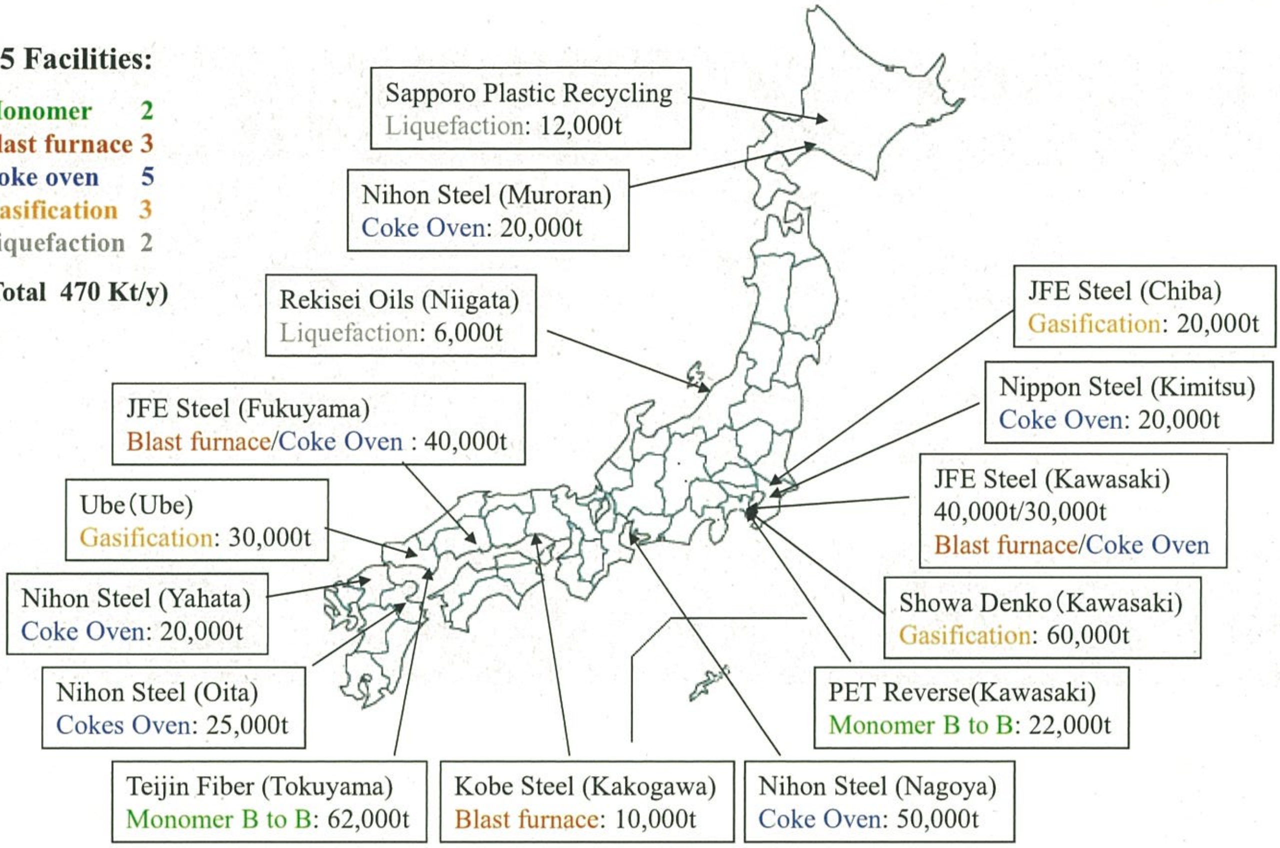
Feedstock Recycling Facilities (-2005)

(complied with C&P recycling law, 2005)

15 Facilities:

Monomer 2
Blast furnace 3
Coke oven 5
Gasification 3
Liquefaction 2

(Total 470 Kt/y)



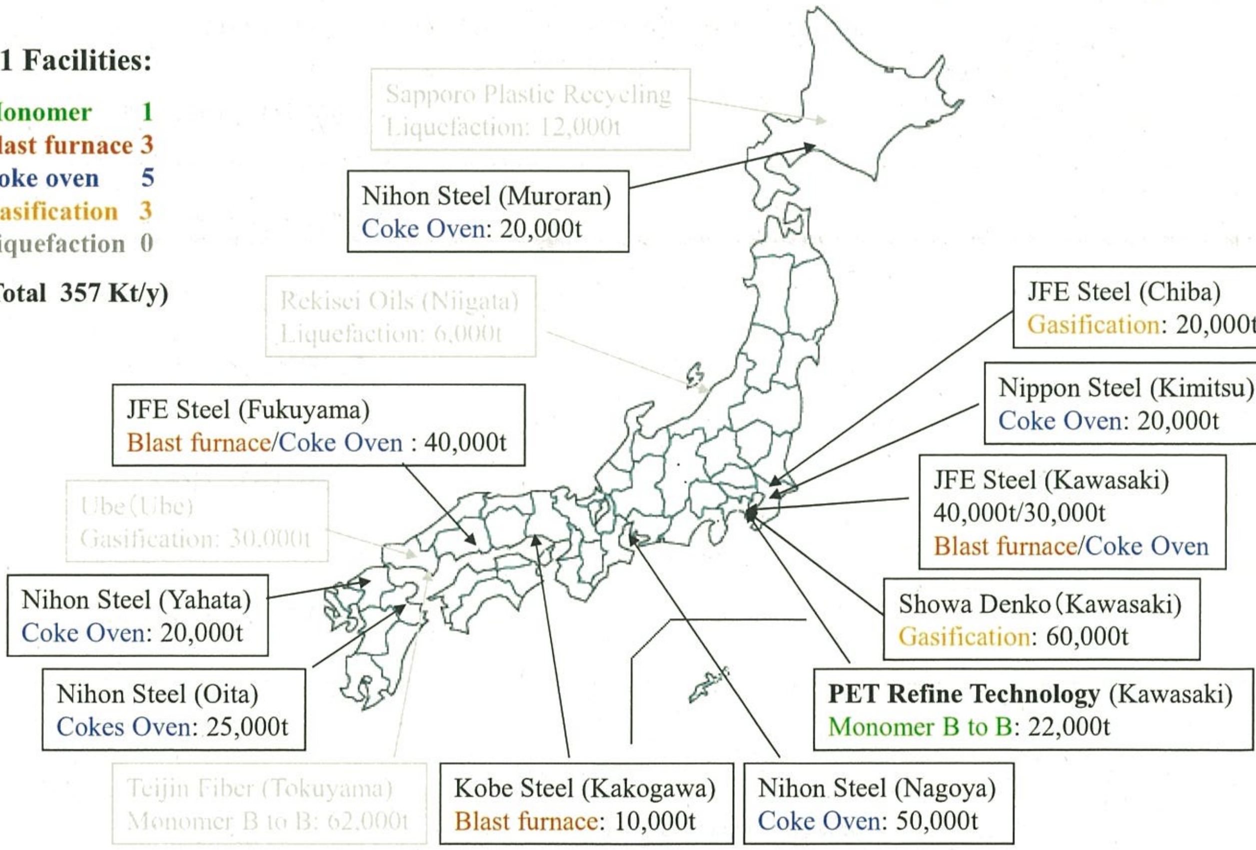
Feedstock Recycling Facilities (-2013)

(complied with C&P recycling law, 2005)

11 Facilities:

Monomer 1
Blast furnace 3
Coke oven 5
Gasification 3
Liquefaction 0

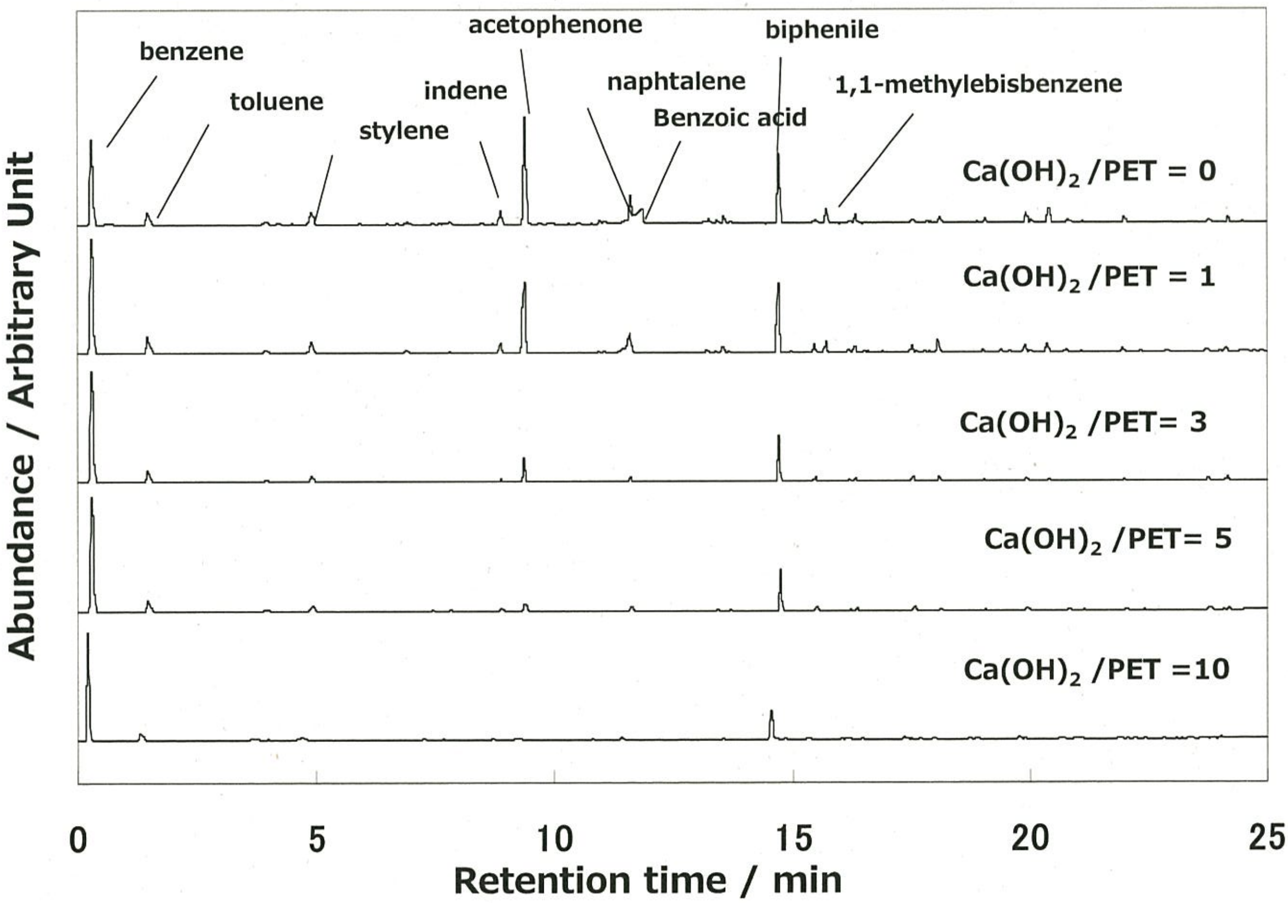
(Total 357 Kt/y)



Amount of contract for each recycling method in 2013

	Categories	Amount (tons)	Share for total (%)	Share for FR (%)
Feedstock	Coke oven	192,503	29	61
	Blast furnace	38,232	6	12
	Gasification	85,463	13	27
	Liquefaction	0	0	0
	Total	316,198	47	100
Mechanical		356,626	53	
Total of CP-P		672,824	100	

Change of products by adding $Ca(OH)_2$ powder and steam



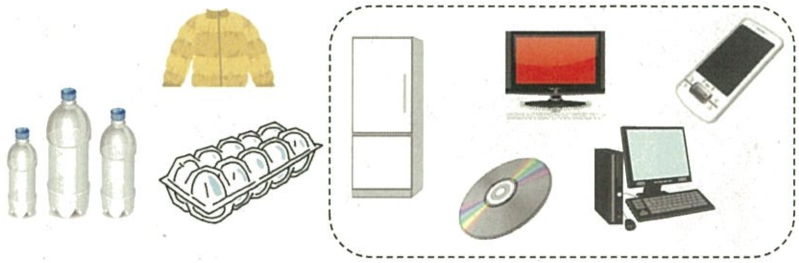
Necessity to recycle both plastics and metals effectively

Plastics

Transparency
Lightweight
Insulation
Chemical resistance

Variety of useful properties

They are widely used in our daily life



Electric and electronic equipments

Plastic-metal composites

Oil and Metal Resources

Rising demand all over the world → concern of supply shortage and depletion is increasing

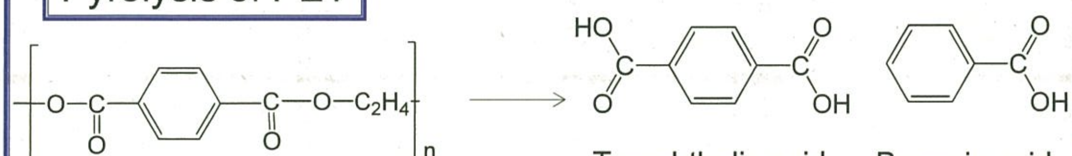
Pyrolysis of poly(ethylene terephtalate)

Poly(ethylene terephthalate) (PET)

PET has useful properties such as transparency and flexibility

It's often used as carrier materials for storage media.

Pyrolysis of PET



PET

Terephthalic acid (TPA)

Benzoic acid (BA)

Sublimating substances

Causing corrosion and clogging of pipes

Unsuitable material for pyrolysis[3)]

Our previous works (steam hydrolysis of PET)

Pyrolysis of PET in the presence of calcium oxide (CaO) or calcium hydroxide ($Ca(OH)_2$)

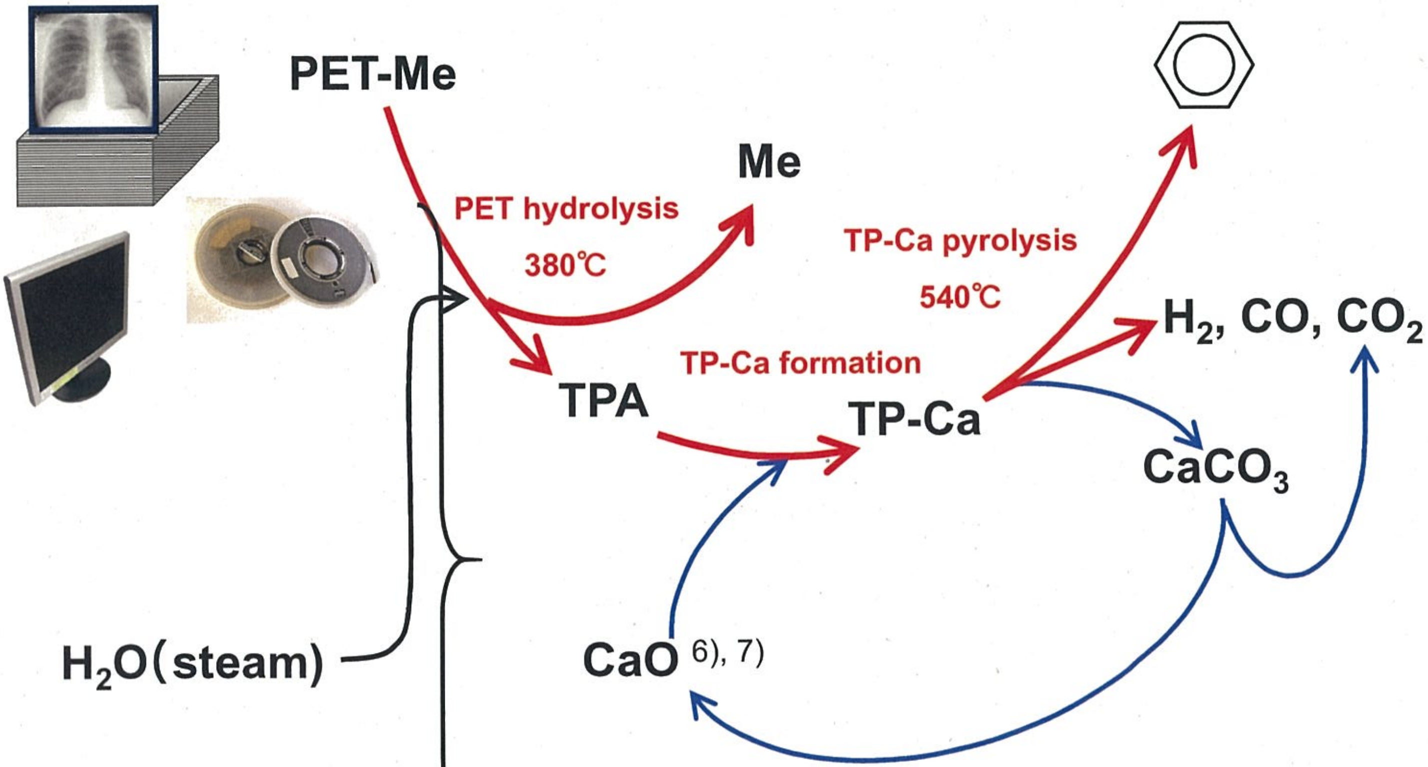
Benzene is obtained selectively without producing sublimating substances[4),5)]

3) Williams, E.A.; Williams, P.T. *J. Chem. Tech. Biotechnol.*, 1997, **70**, 9-20.

4) T. Yoshioka, E. Kitagawa, T. Mizoguchi, A. Okuwaki. *Chem. Lett.* 2004, **33**, 282.

5) G. Grause, T. Handa, T. Kameda, T. Mizoguchi, T. Yoshioka. *Chem. Eng. J.* 2011, **166**, 523.

Benzene production and metal recovery flow

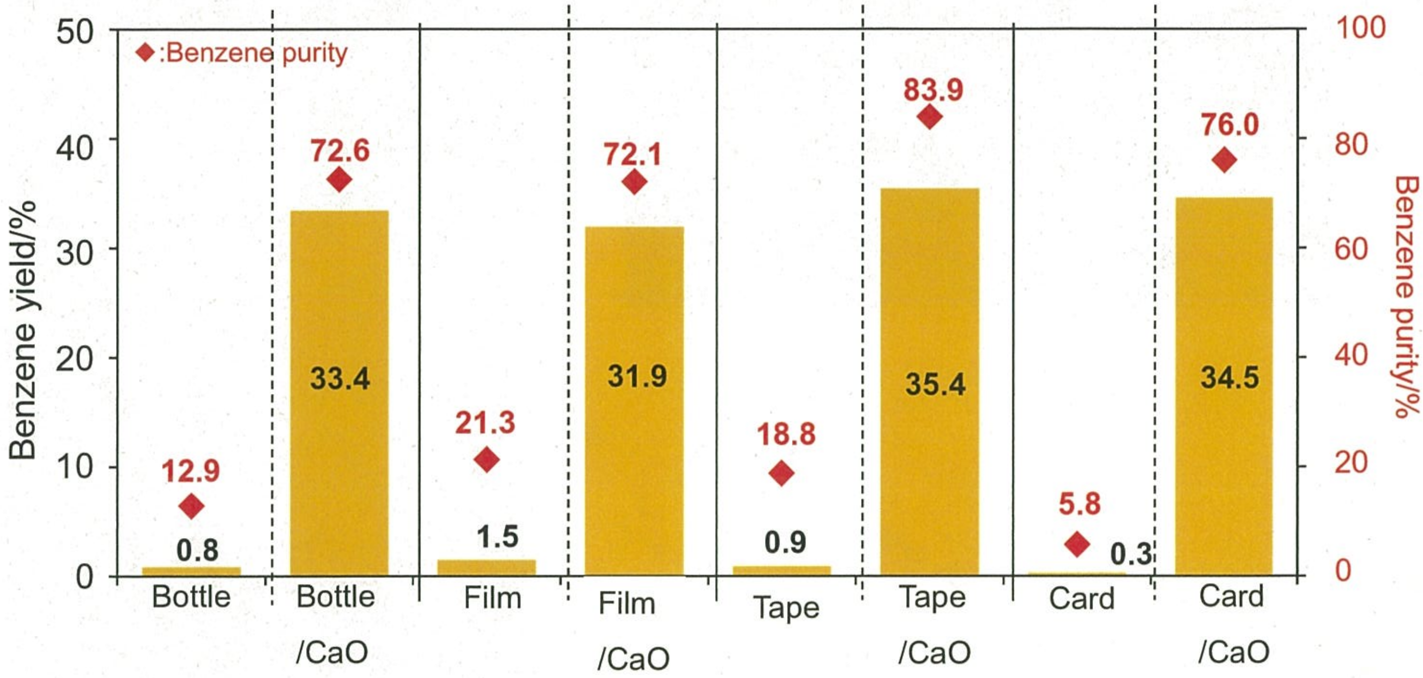


6) S. Kumagai, G. Grause, T. Kameda, T. Takano, H. Horiuchi, T. Yoshioka. *Ind. Eng. Chem. Res.* 2011, **50**, 1831.
7) S. Kumagai, G. Grause, T. Kameda, T. Takano, H. Horiuchi, T. Yoshioka. *Ind. Eng. Chem. Res.* 2011, **50**, 6594.

PET分解物生成物分布

雰囲気（He or steam）	He	steam	steam
温度[℃]	700	700	500
試料	PET：CaO	PET：Ca(OH)2	PET：CaO(固定層)
Oil 組成 [wt%]			
benzene	46.6	70.1	83
toluene	5.3	5.3	3.1
ethylbenzene	1.2	0.6	1.9
styrene	4.9	3	0.6
indene	23.2	0.7	0.3
acetophenone	3.7	4.7	0.3
naphthalene	6	1.2	0.3
biphenyl	2.2	11.7	7.8
4-methylbiphenyl	1.3	1	0.3
1,2-diphenylethylene	0.9	0.7	0.3
fluorene	0.8	1	0.3
phenantrene	1.1		0.3
antracene	2.8		0.3
4-phenylmethylbiiphenyl			0.6
7-methylbenzantracene			0.3
12-methylbenzantracene			0.3
Total	100	100	100
Gas 組成 [wt%]			
Hydrogen	2.3	4.3	10.1
Methane	5.1	7.4	34.8
Ethylene	3.4	3.7	5.6
Ethane	0.4	1.3	0
Carbon monoxide	58.3	14.5	7.9
Carbon dioxide	30.5	68.8	41.6
Total	100	100	100
重量比（Oil：Gas）	0.63：1.00	0.73：1.00	3.57：1.00

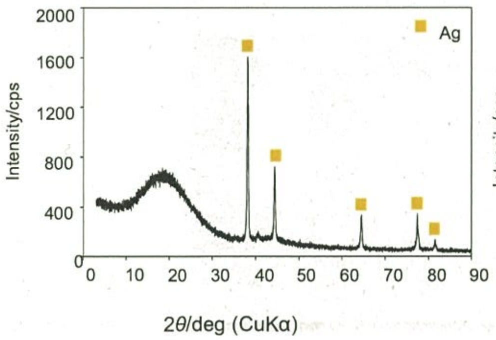
Benzene yield & purity in the presence and absence of CaO

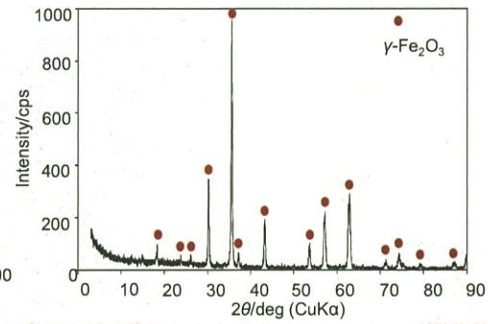


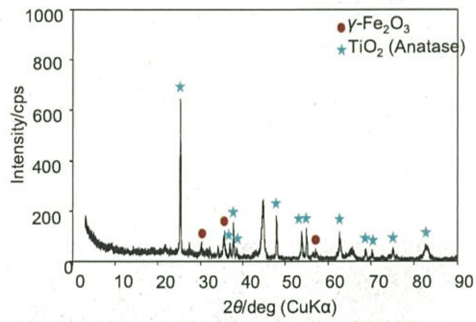
Presence of CaO:

Benzene yield and purity drastically improved by CaO addition

Metal recovery from some composite materials







Hydrolysis temp. 450 ºC, steam 88 vol%

Ag recovery

over 94%

Residue composition

Ag : 3%

Carbon:97%

Ag concentrated from the initial 0.4 wt% to 3 wt%

X-ray film

γ-Fe_2O_3 recovery

over 96%

No transformation to α type

Residue composition

γ-Fe_2O_3:66% (Fe:46%)

Carbon:34%

Video tape

γ-Fe_2O_3 recovery TiO$_2$ recovery

over 96% **over 87%**

No transformation was observed

Al_2O_3 recovery

Almost quantitatively recovered

Residue composition

γ-Fe_2O_3:37%

TiO_2:35%

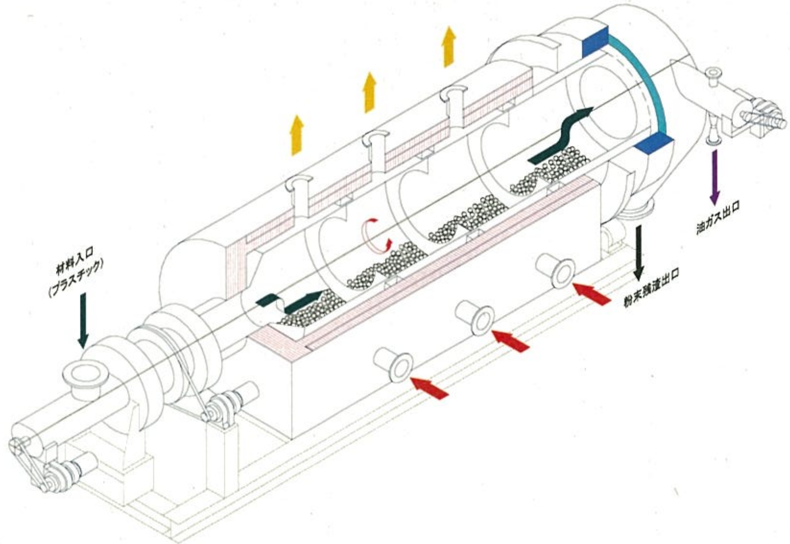
Al_2O_3:2%

Carbon:26%

It might become an ilmenite substitute (TiO_2: 45～60%)

Prepaid card

Liquefaction plant of PET pyrolysis



Product oil and recovered Ag from waste X-ray film

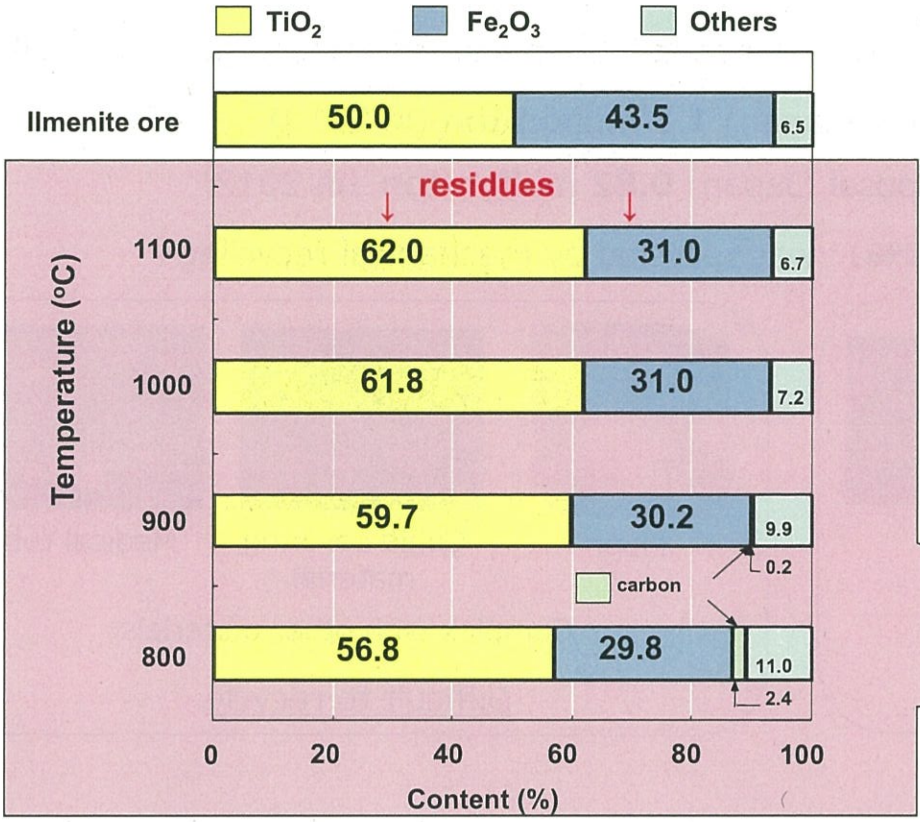
raw materials (X-ray film)

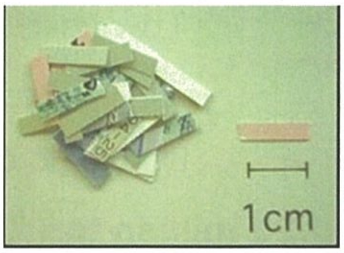
Product oil (main: Benzene)

Recovered Ag

(recovered 96%, purity 99.33

Comparison of the composition of residues with ilmenite





Recovery of TiO_2 by Manufacturing process (Sulfate process)

Solution

$$FeTiO_3 + 2H_2SO_4$$

(illumenite)

$$\rightarrow TiOSO_4 + FeSO_4 + 2H_2O$$

Hydrolysis

$$TiOSO_4 + 2H_2O$$

$$\rightarrow TiO(OH)_2 \downarrow + H_2SO_4$$

Calcination

$$TiO(OH)_2 \rightarrow TiO_2 + H_2O$$

Anatase or Rutile

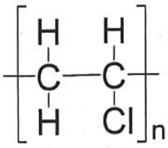
from prepaid card **from ilmenite**

Table Degree of TiO_2 leached from residues

Temperature (°C)	800	900	1000	1100	illumenite
Leaching ratio of TiO_2 (%)	100.0	100.0	96.4	72.3	46.4

conc.-H_2SO_4 at 220 °C

PVC



Low cost, good machinability, Chemical resistance, good durability

Production (Japan) **1.5 million ton** (in 2013)

Domestic disposal (Japan) **0.82 million ton** (in 2012)

0.23 million ton (28%) was recycled by mechanical recycling[1)]

Pipes

Film

Stable component

Easy to recycle

Floor

Cable covering material

Medical tube

Complex with other materials

Difficult to recycle

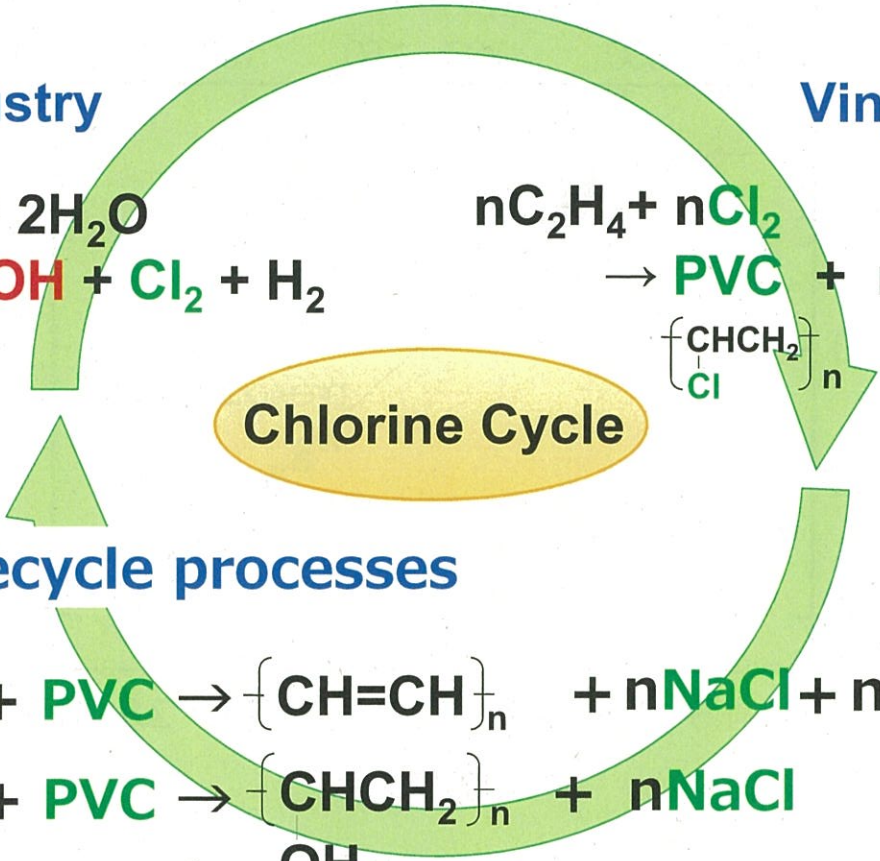
1) Plastic Waste Management Institute, Plastic Products, Plastic Waste and Resource Recovery (2012).

Alkali Industry (Electrolysis of table salt process)

Alkali industry = Chlorine production

$$2NaCl + 2H_2O \rightarrow 2NaOH + Cl_2 + H_2$$

Chlorine Cycle processes



Alkali industry

$2NaCl + 2H_2O$
$\rightarrow 2NaOH + Cl_2 + H_2$

Vinyl industry

$nC_2H_4 + nCl_2$
$\rightarrow PVC + nHCl$

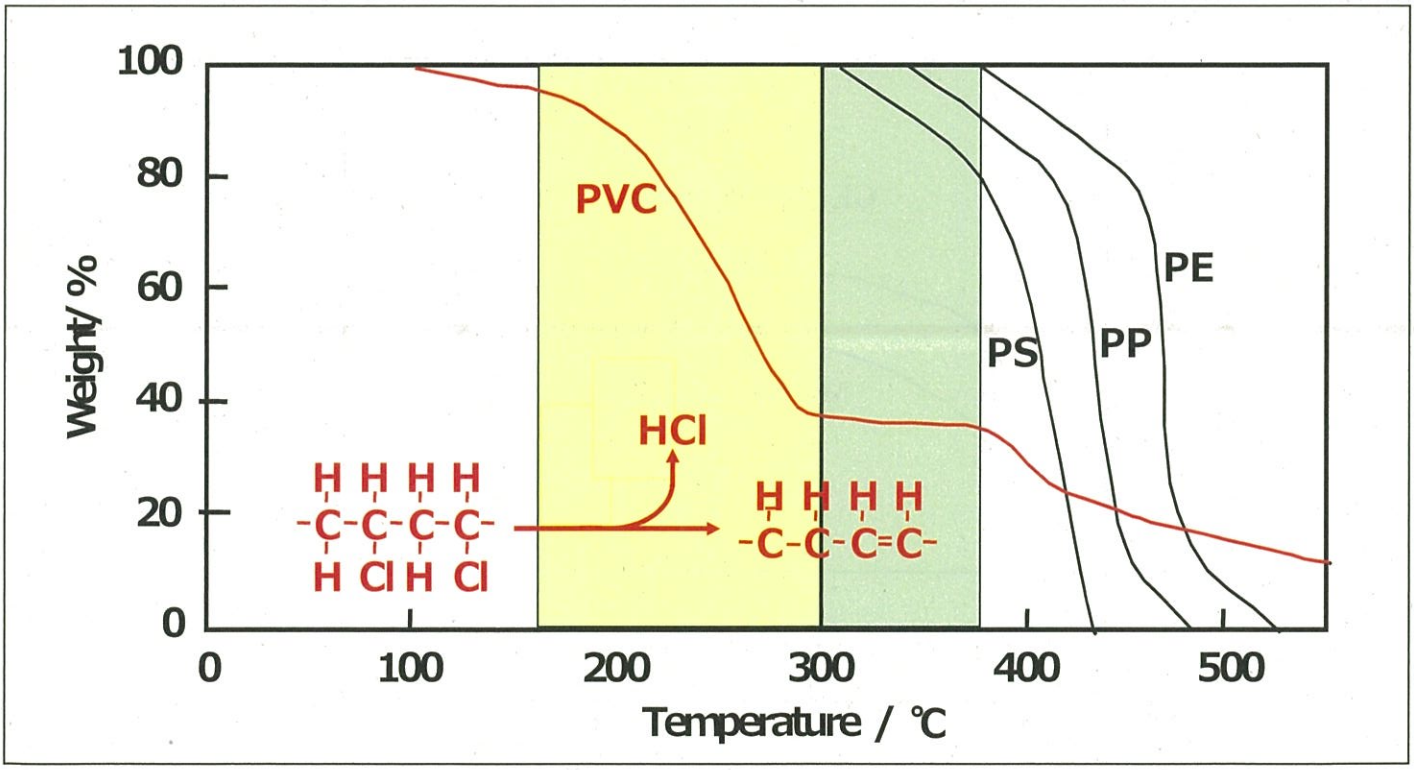
$\left[\underset{\substack{| \\ Cl}}{C}HCH_2 \right]_n$

Recycle processes

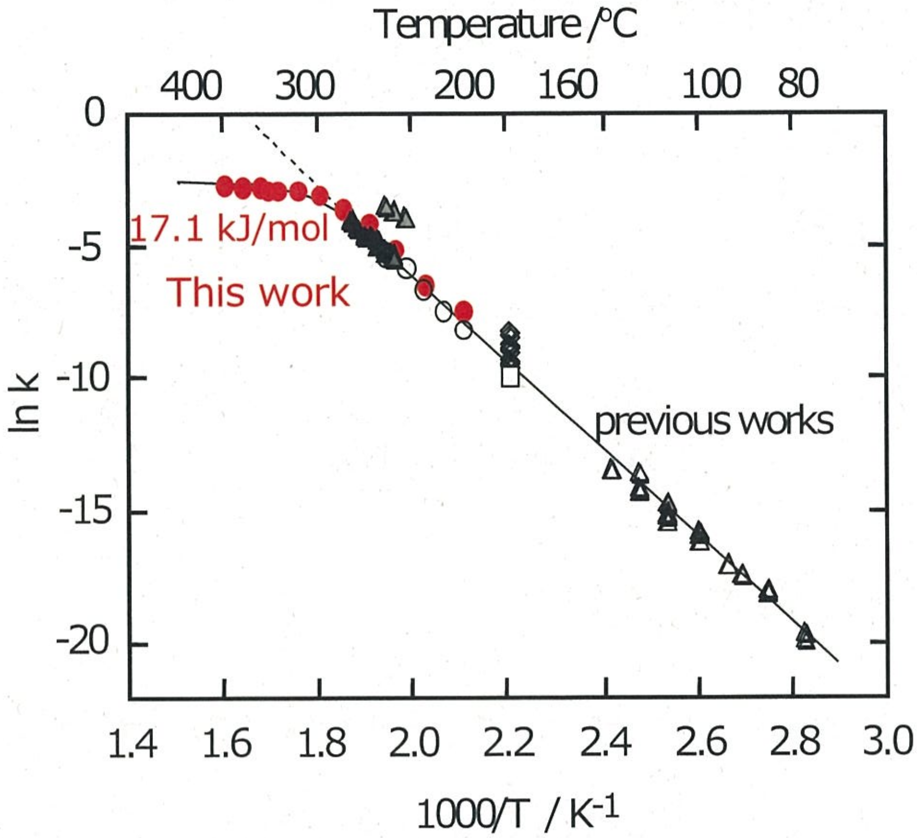
$nNaOH + PVC \rightarrow \left[CH{=}CH \right]_n + nNaCl + nH_2O$

$nNaOH + PVC \rightarrow \left[\underset{\substack{| \\ OH}}{C}HCH_2 \right]_n + nNaCl$

PVCの熱分解挙動

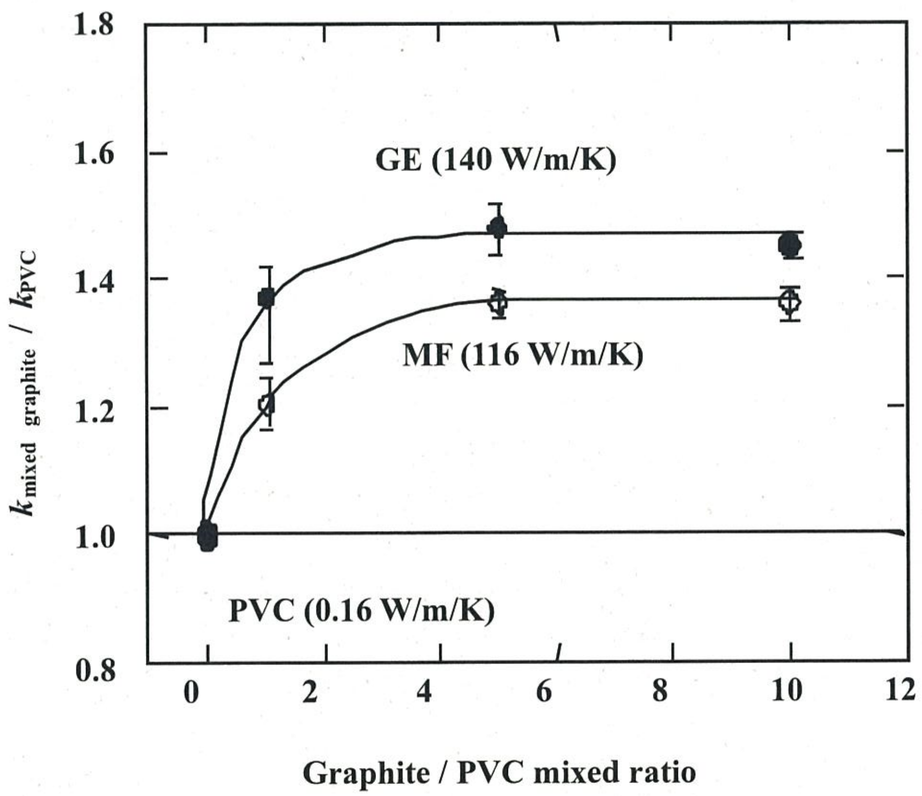


PVC脱塩化水素の温度依存性



T.Yoshioka, N.Saitoh, A.Okuwaki, *Chemistry Letters*, **34**, No.1 (2005), 70-71

PVCの脱塩化水素に及ぼす黒鉛添加の影響



T.Yoshioka, N.Saitoh, A.Okuwaki, *Chemistry Letters*, **34**, No.1 (2005), 70-71

廃プラスチック(PVC)の脱塩素装置の概略

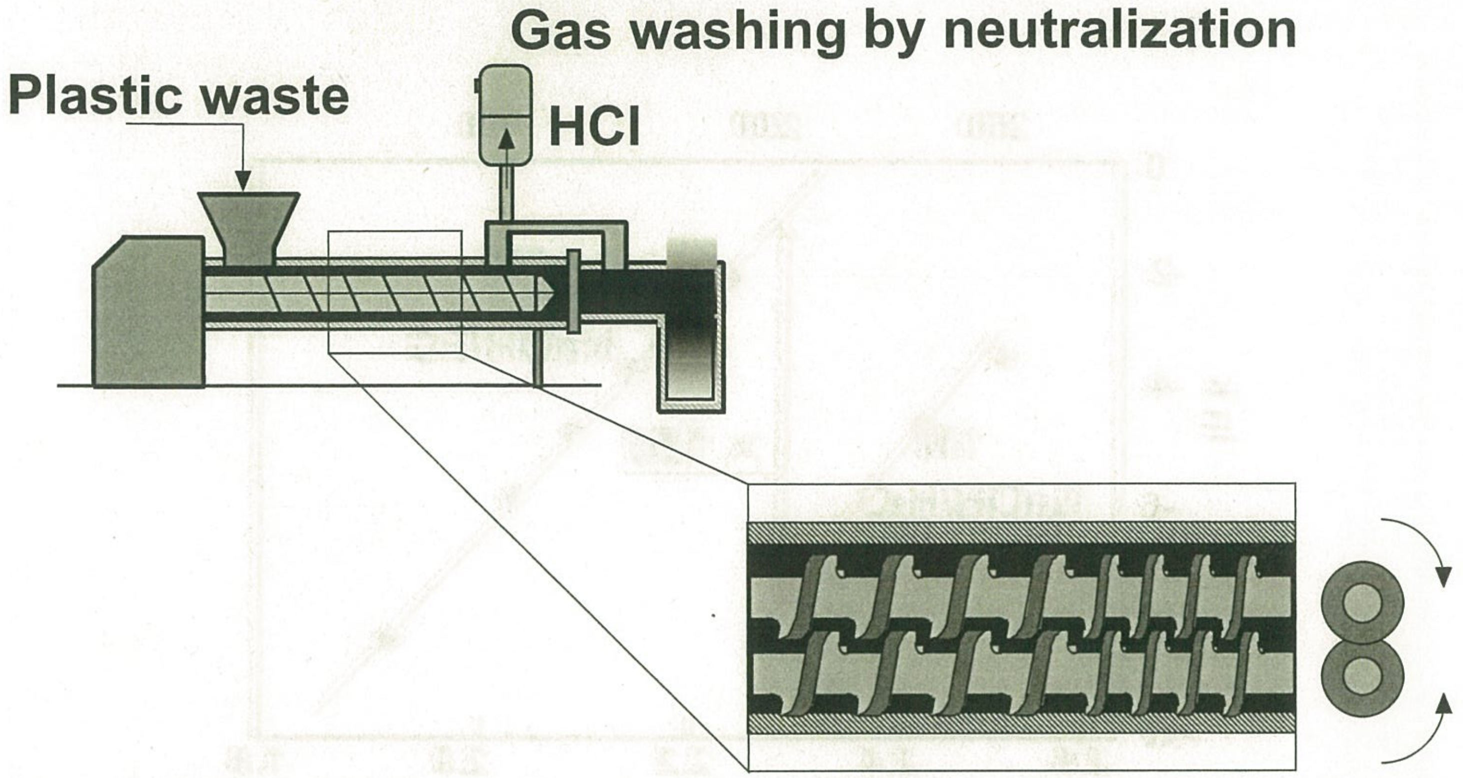


Fig. Counter-rotating twin-screw extruder

Dechlorination (≠ Dehydrochlorination) of PVC

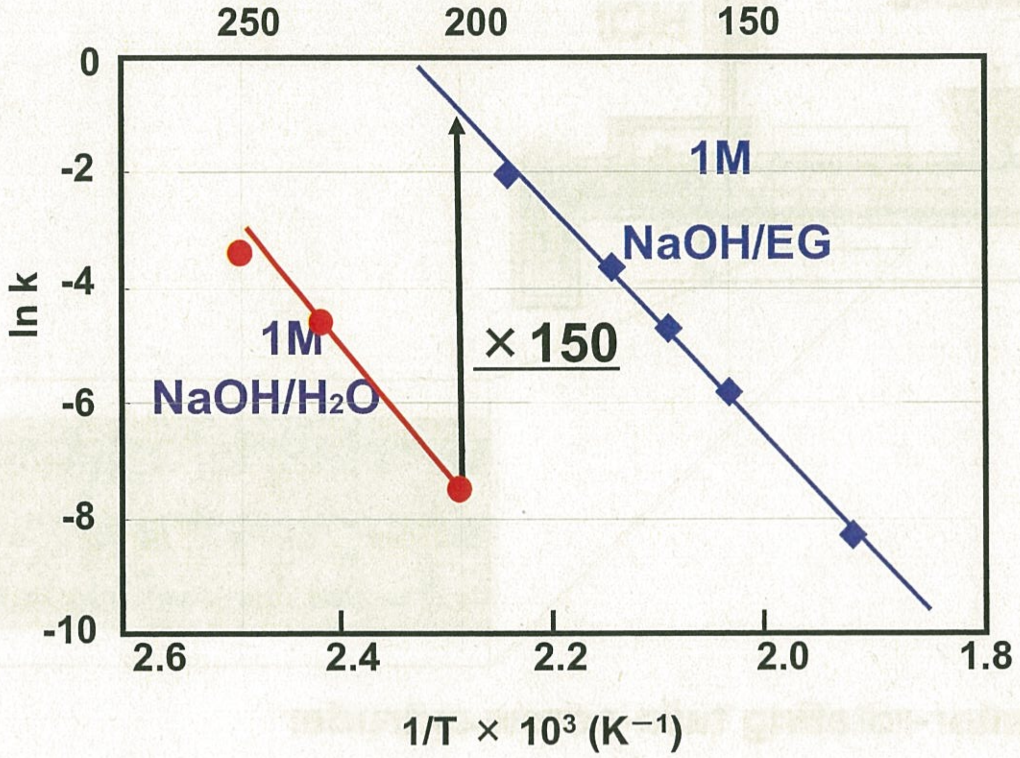
E2 elimination

$$n\text{NaOH} + \text{PVC} \rightarrow \left[\text{CH=CH}\right]_n + n\text{NaCl} + n\text{H}_2\text{O}$$

Sn2 substitution

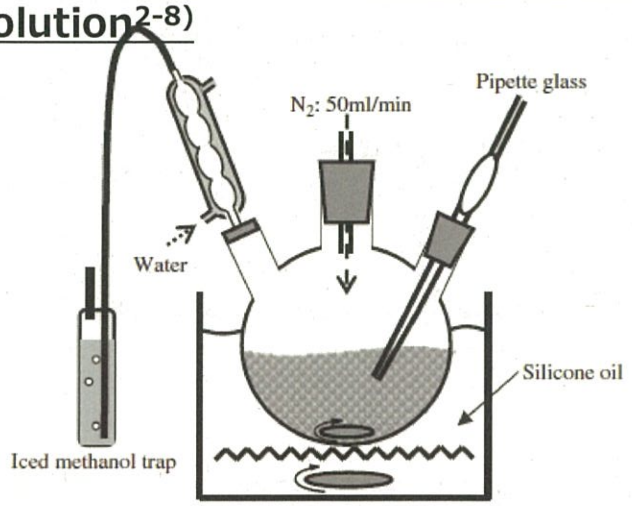
$$n\text{NaOH} + \text{PVC} \rightarrow \left[\underset{\text{OH}}{\text{CH}}\text{CH}_2\right]_n + n\text{NaCl}$$

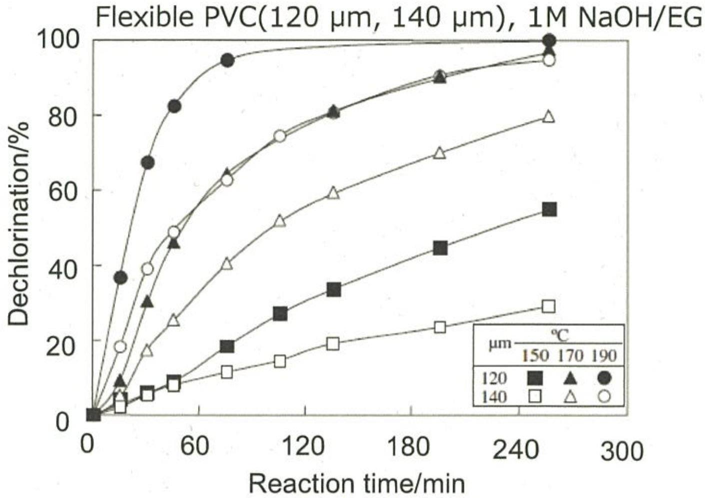
Dechlorination in NaOH/EG



Dechlorination of PVC

Dechlorination of PVC in NaOH/EG solution[2-8]





2) Yoshioka et al., *Polym. Degrad. Stab.*, **93**, 1183 (2008). 3) Yoshioka et al., *Polym. Degrad. Stab.*, **93**, 1822 (2008).
4) Yoshioka et al., *Polym. Degrad. Stab.*, **94**, 1995 (2008). 5) Osada et al., *J. Mater. Cycles Waste Manag.*, **11**, 19 (2009).
6) Yoshioka et al., *J. Polym. Res.*, **17**, 489 (2010). 7) Kameda et al., *Polym. Degrad. Stab.*, **95**, 2663 (2010).
8) Kameda et al., *J. Polym. Res.*, **18**, 1687 (2011).

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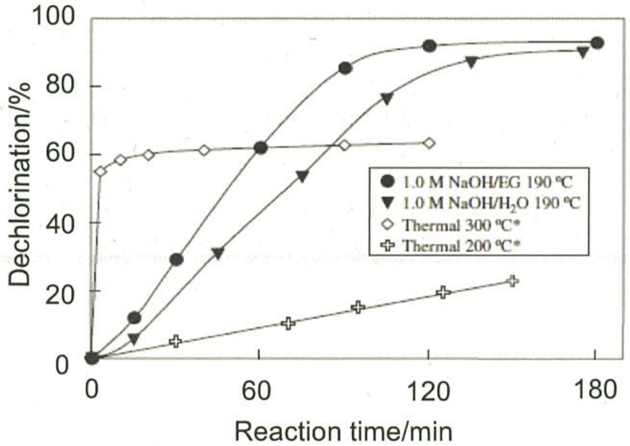
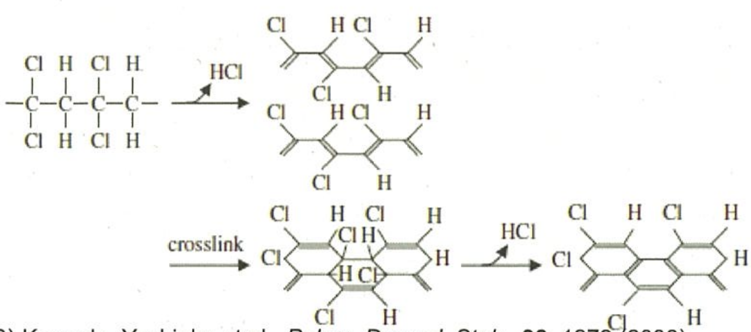
Dechlorination of other chlorine containing materials

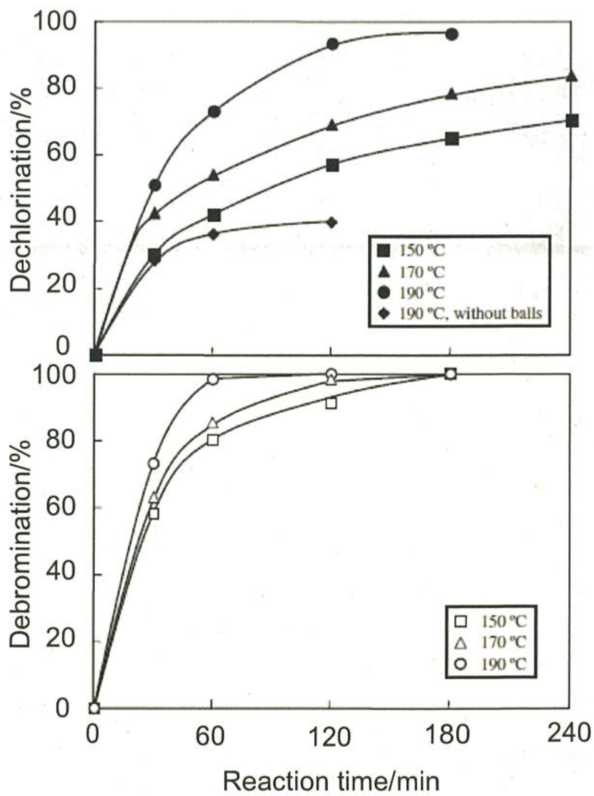
Poly(vinylidene chloride)[9]



Dehydrochlorination of PVDC (thermal)[10]



Automobile Shredder Dust[11]



9) Kameda, Yoshioka et al., *Polym. Degrad. Stab.*, **93**, 1979 (2008).
10) Shun et al., *Polym.Sci. Polym. Chem. Ed.*, **23**, 1193 (1985). 11) Kameda, Yoshioka et al., *Chemosphere*, **74**, 287 (2009).

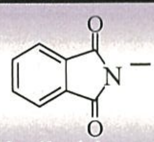
Addition of new function group (Nu) into PVC by substitution of Cl

Sn2 substitution

$$\left[CH_2-\underset{\displaystyle Cl}{CH} \right]_n + Nu^- \longrightarrow \left[CH_2-\underset{\displaystyle Nu}{CH} \right]_n + Cl^-$$

Ex) Nucleophiles

I^- , SCN^- , OH^- , N_3^- ,



phthalimide anion

Effects by the Chemical Modification

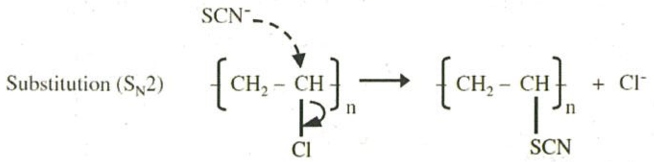
Modifying group	Long-carbon chain	Hydrophilic group	Epoxy group	Cross-link [1]	SCN group [2]
Function	Plasticity	Hydrophilicity	High reactivity	Heat-resistant Mechanical characteristic	Antibacterial

$$\left[CH_2-\underset{\displaystyle Cl}{CH} \right]_n + Nu^- \xrightarrow{\text{Base}} \left[CH_2-\underset{\displaystyle Nu}{CH} \right]_m \left[CH_2-\underset{\displaystyle Cl}{CH} \right]_{n-m} + mCl^-$$

1) M. Hidalgo, H. Reinecke, C. Mijangos, *Polymer,* **40**, 3535, (1999).
2) T. Kameda, M. Ono, G. Grause, T. Mizoguchi, T. Yoshioka, *J Polym Res.*, **18**, 945, (2011).

Upgrading Recycling of PVC[12-17)]

Introduction of function group by S_N2 reaction



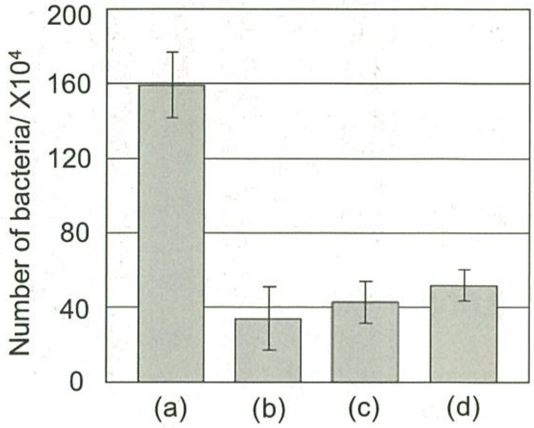
Antibacterial grant by the introduction of the thioiocyanate group

Sample	*S* (%)	*E* (%)	FT–IR spectra: thiocyanate	FT–IR spectra: isothiocyanate	solvent
(a) PVC	—	—	×	×	
(b) SCN–PVC	3.8	0.4	×	○	THF–DMSO
(c) SCN–PVC	18.7	10.2	○	○	DMF
(d) SCN–PVC	3.8	1.0	○	○	H_2O + TBAB

for Staphylococcus

Thiocyanate group : -S-C≡N

Isocyanate group : -N=C=S



12) Kameda et al., *Polym. Degrad. Stab.*, ***94***, 107 (2009). 13) Kameda et al., *Mat. Chem. Phys.*, ***118***, 362 (2009).
14) Kameda et al., *Mat. Chem. Phys.*, ***124***, 163 (2010). 15) Kameda et al., *J. Polym. Res.*, **18**, 945 (2011).
16) Yoshihara et al., *J. Mater. Cycles Waste Manag.*, **12**, 264 (2010). 28) Kameda et al., *Polym. Eng. Sci.*, **51**, 1108 (2011).
17) Grause et al., *J.Mater. Cycles Waste Manag.*, in press.

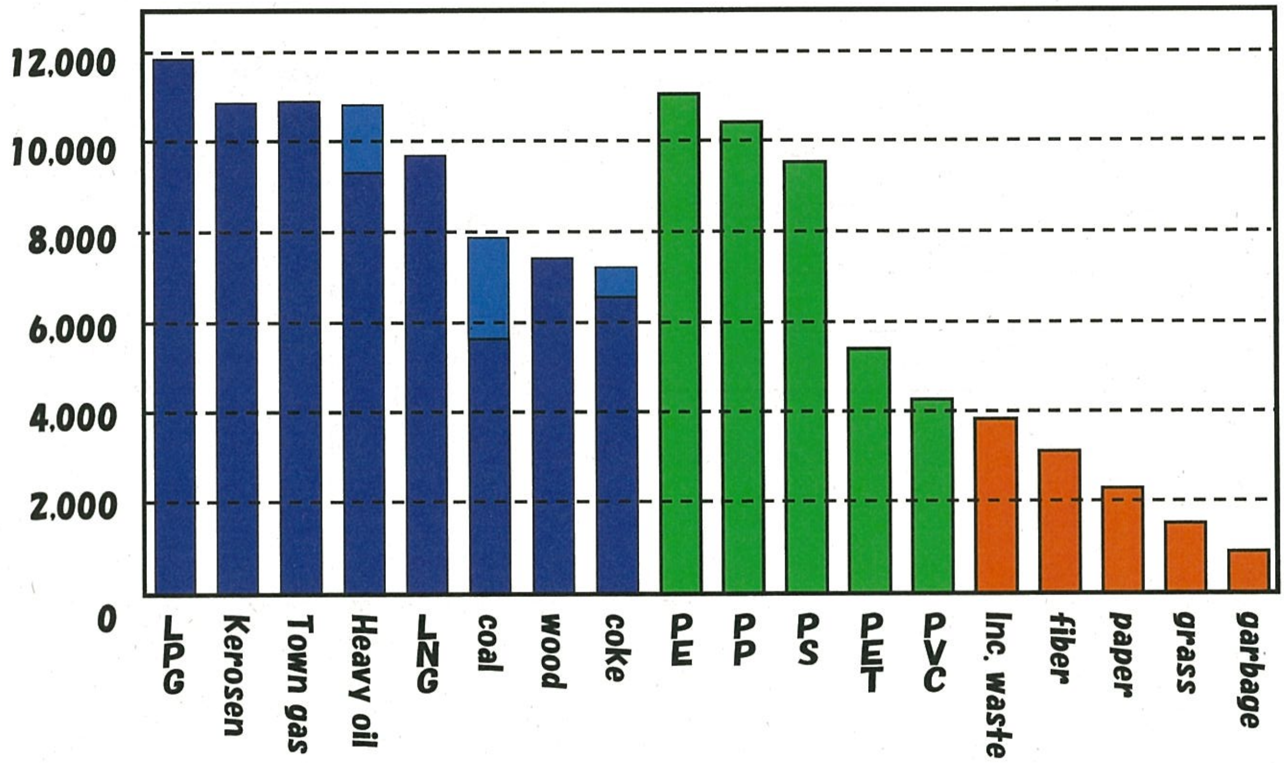
The amount of waste plastics and energy

	The amount of waste (million tons)	Energy capacity (kcal)
total	8.84	8.13 x 10^{13}
none use	6.63	6.08 x 10^{13}
landfill	3.36	3.08 x 10^{13}
incineration	3.27	3.00 x 10^{13}

CO_2 emission from waste plastics for none use

→ **20 million tons**

Energy capacities of belongings

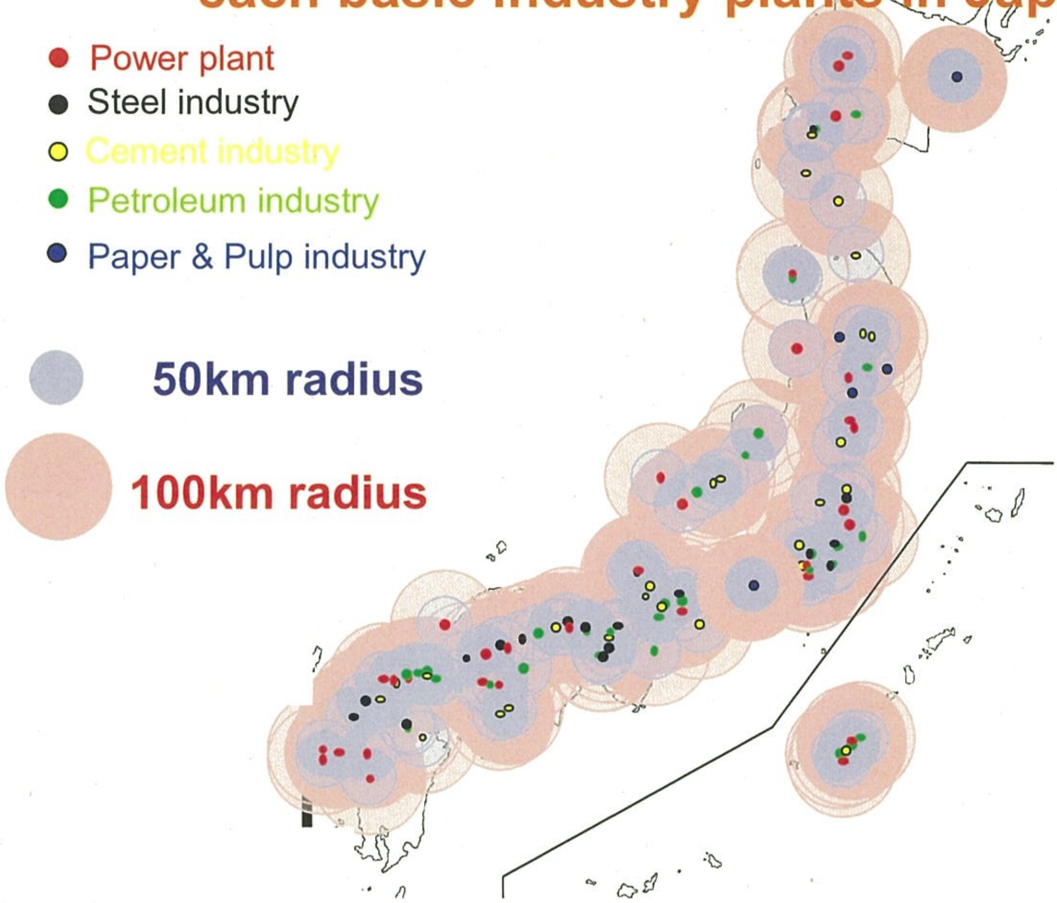


CO_2 discharge in key industries by usage of waste plastics

The case of using for none use waste plastics

	coal consumption	CO_2 emission	reduction of CO_2	(ratio)
	million tons	million tons	million tons	(%)
Power generation	43.34	119.19	77.82	6.5
Steel	86.01	268.06	82.72	3.1
Cement	8.54	26.71	7.78	28.8

Circles of 50km and 100km radius around the each basic industry plants in Japan



Thank you for your attention!