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Study of Chemical Recycling Technology from waste PS to Styrene Monomer

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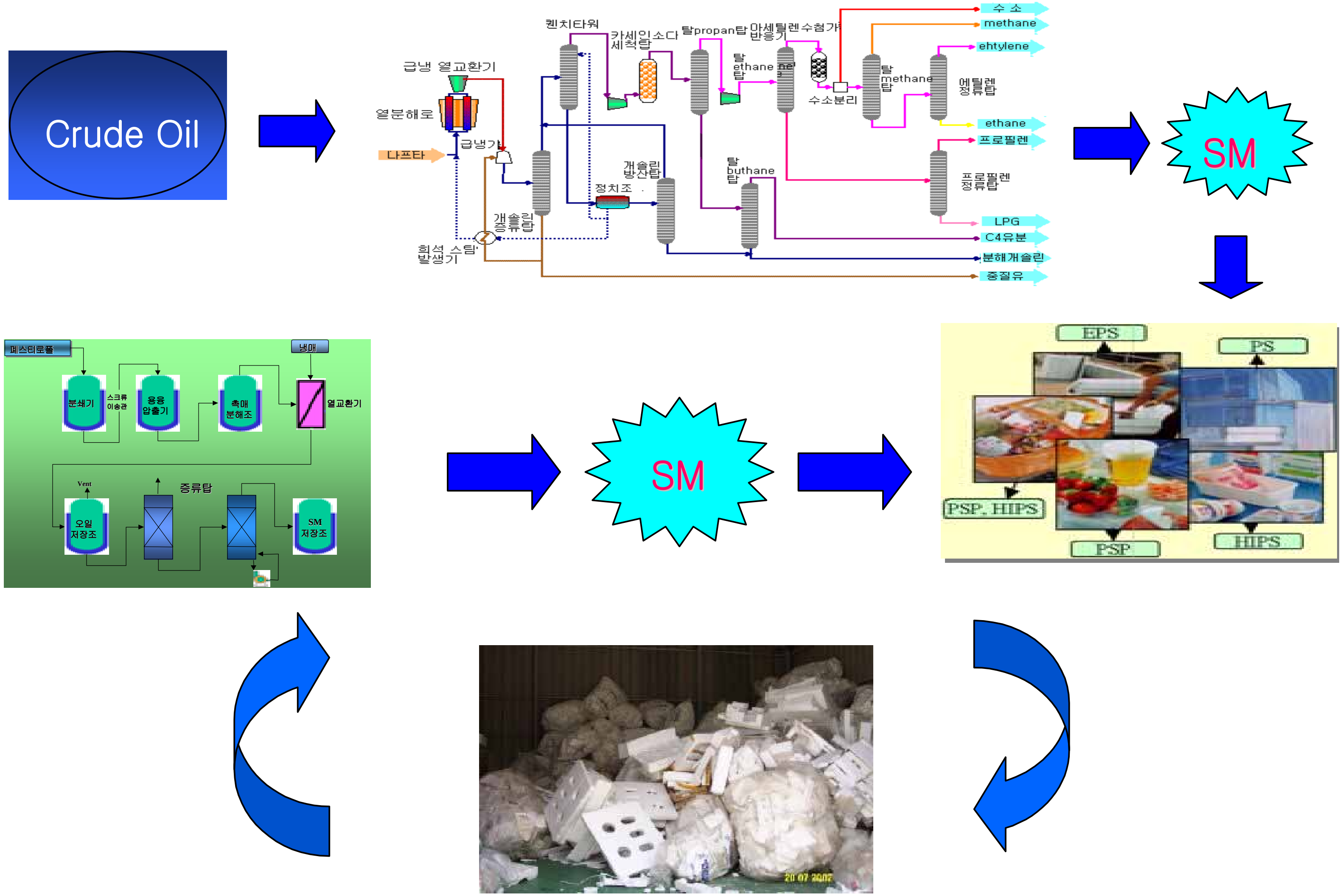
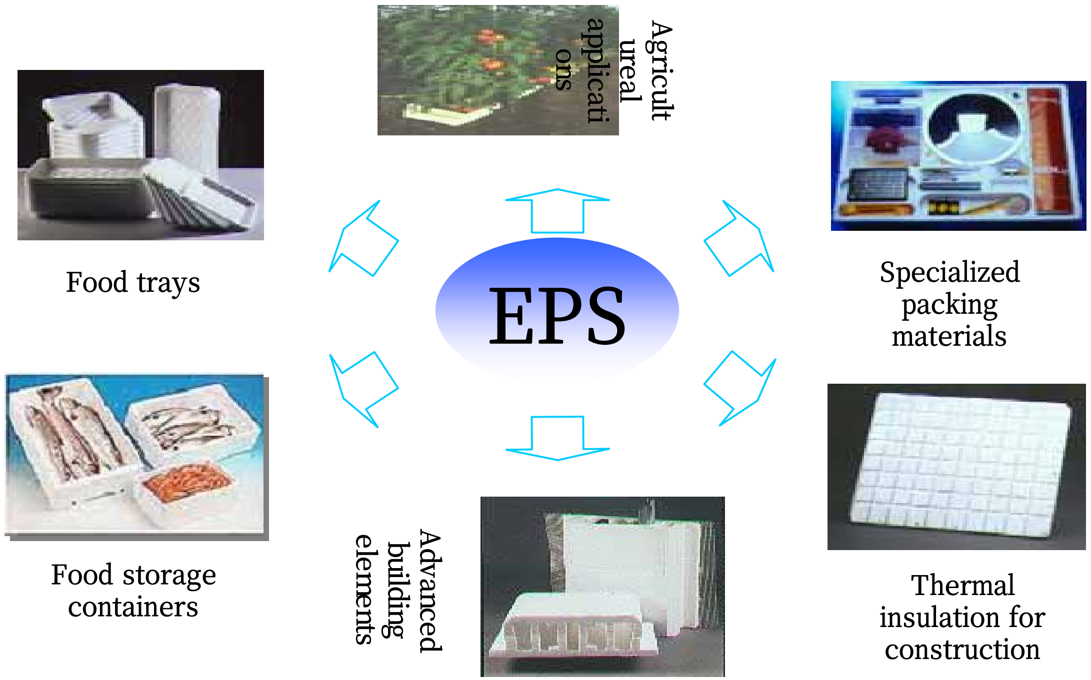
Flow cycle for Chemical Recycling of Polystyrene



Waste Expandable Polystyrene

Annual generation amount:
49,529 ton/year



Recycling according to discharge source (%)

Unit : ×1,000 ton

	House hold	Vegetable market	Depart -ment	Super market	Electricity/ electronic	General enterprise	Others	Total
Generation	8.35	8.43	7.97	8.24	5.83	6.48	4.22	49.53
Recycling	5.48	4.47	4.89	5.85	3.59	3.42	1.64	29.34
%	65.6	53.0	61.4	71.0	61.5	52.7	38.9	59.2

Korea Foam-Styrene Recycling Association (2003)

Recycling Uses

Recycling Resin

Picture Frame

Bathroom footing

Synthesis Wood

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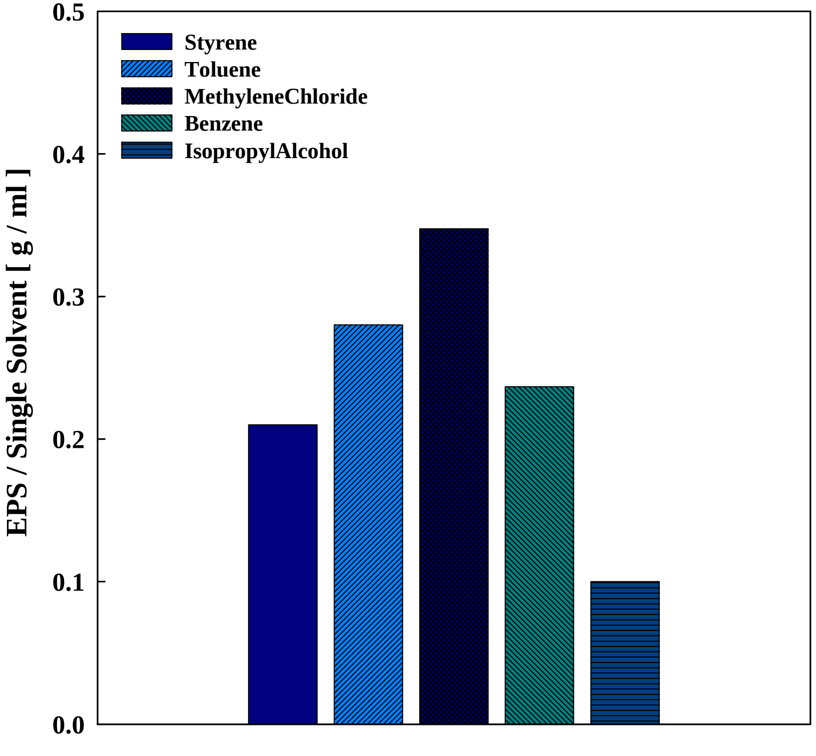
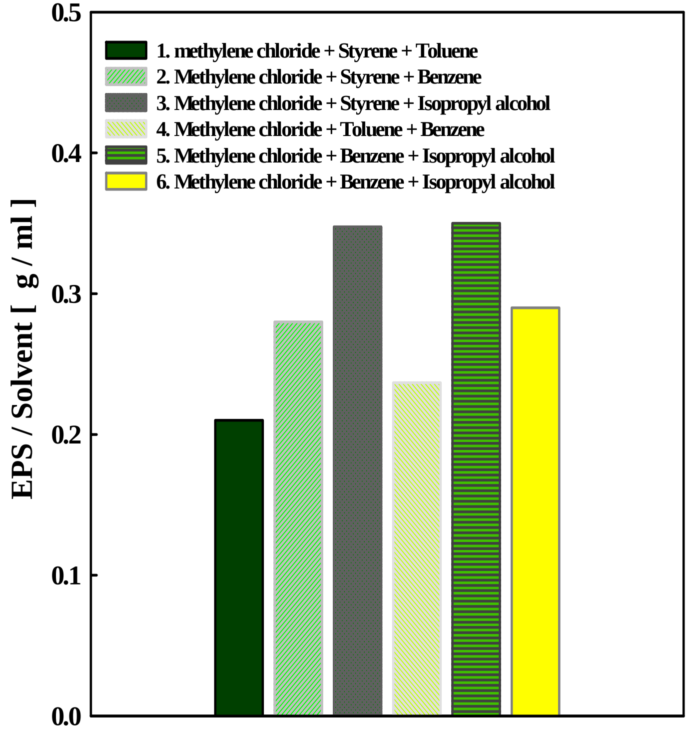
Waste Floating Polystyrene

Dissolution Factors : Type of Solvent, Shape/Size, Solubility, Impurity

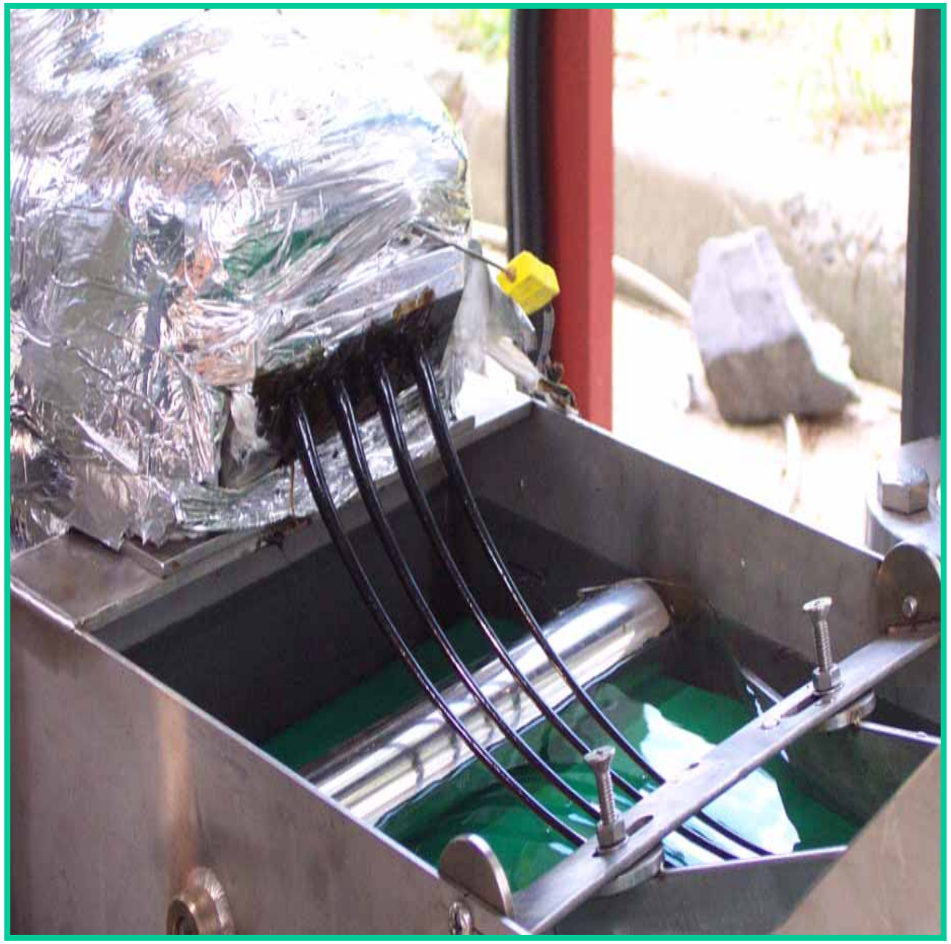
Comparison on Solubility of EPS for Various Solvents

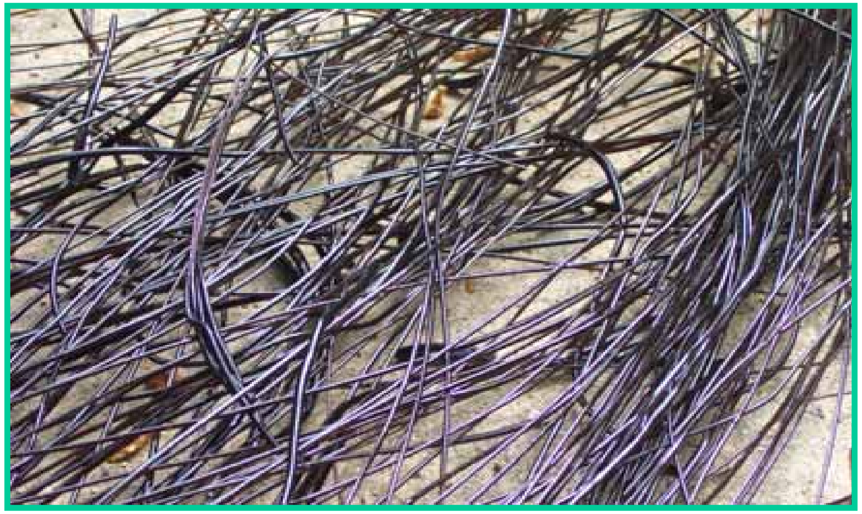




Apparatus for Feed Preparation from WFEPS

Experiments - PS Discharge Rate & Thickness





Motor (rpm)	Discharge rate (kg/hr)
10	12
15	18.1
20	27.3
30	40.5

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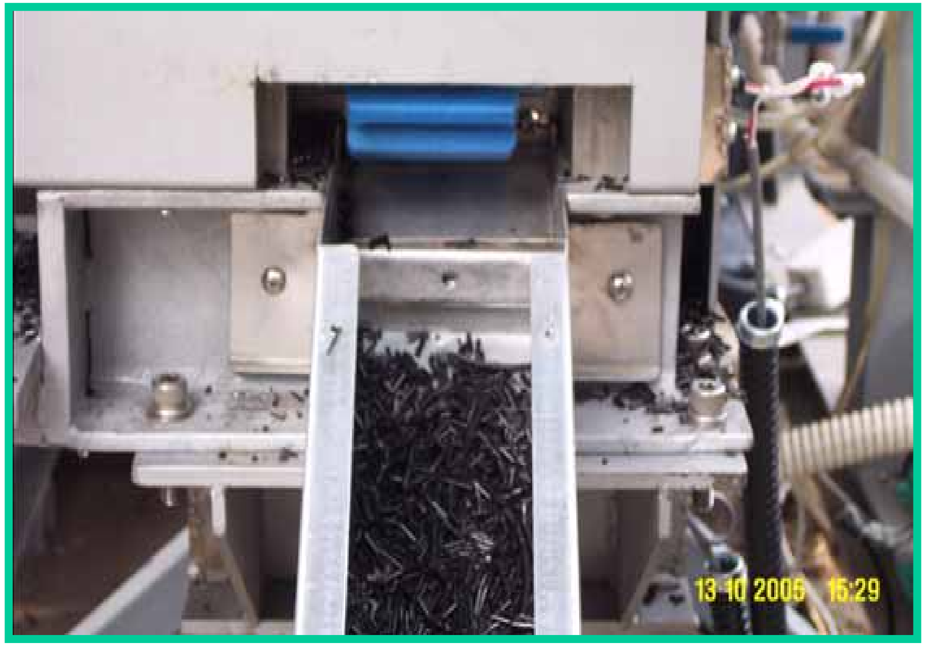
Experiments - Pellet Dia. / Rotation



Roller (rpm)	Pellet Dia. (mm)
60	2.7
70	2.7
80	2.3
90	1.9
100	1.6

Extruder Motor 10 rpm, 170℃

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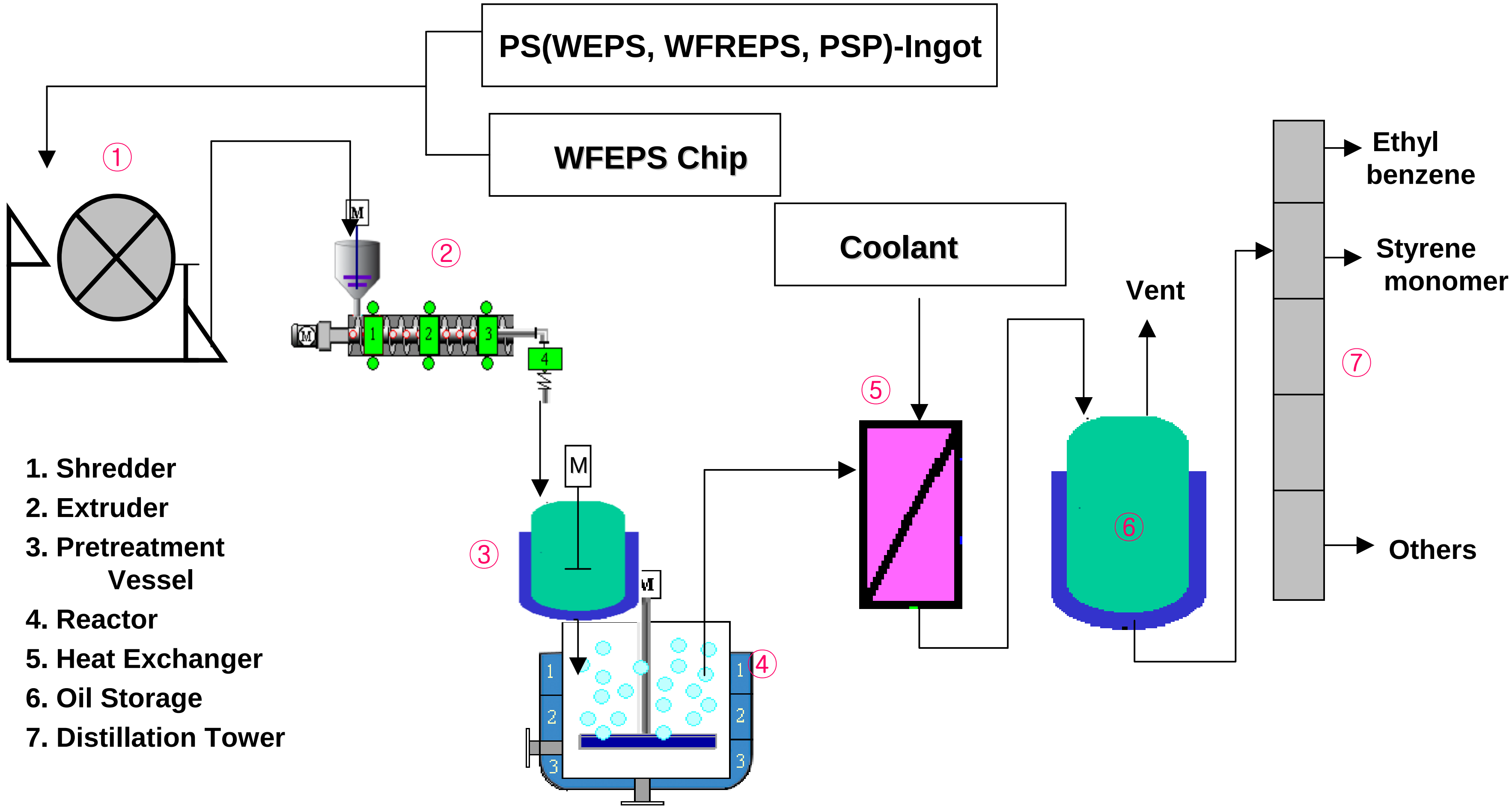
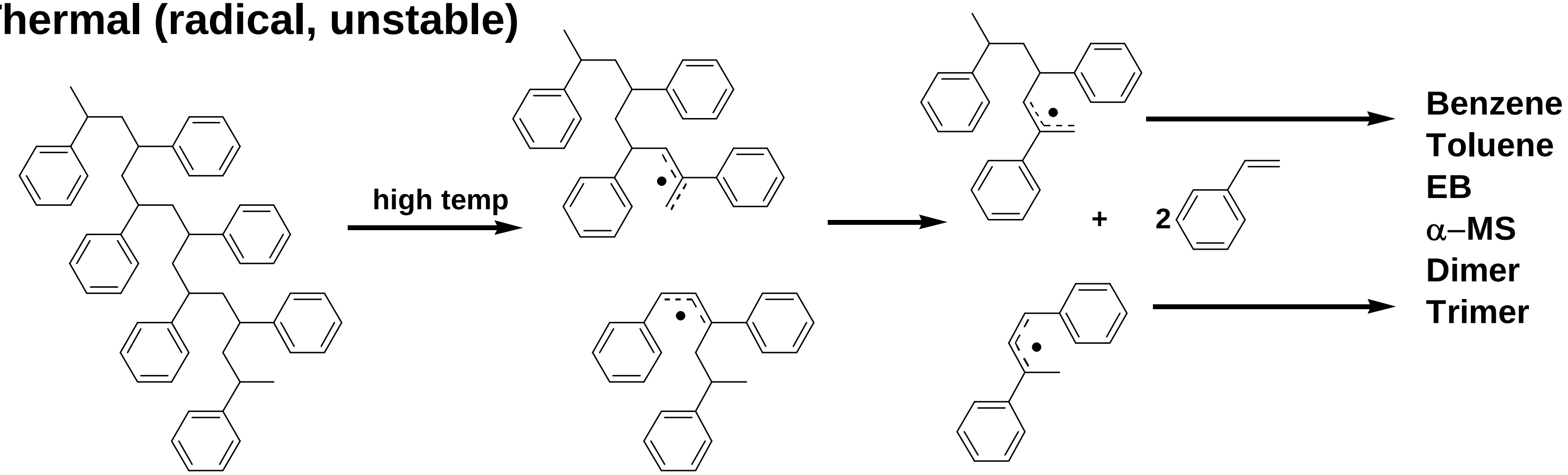
Conceptual Process Flow Sheet – WEPS to SM



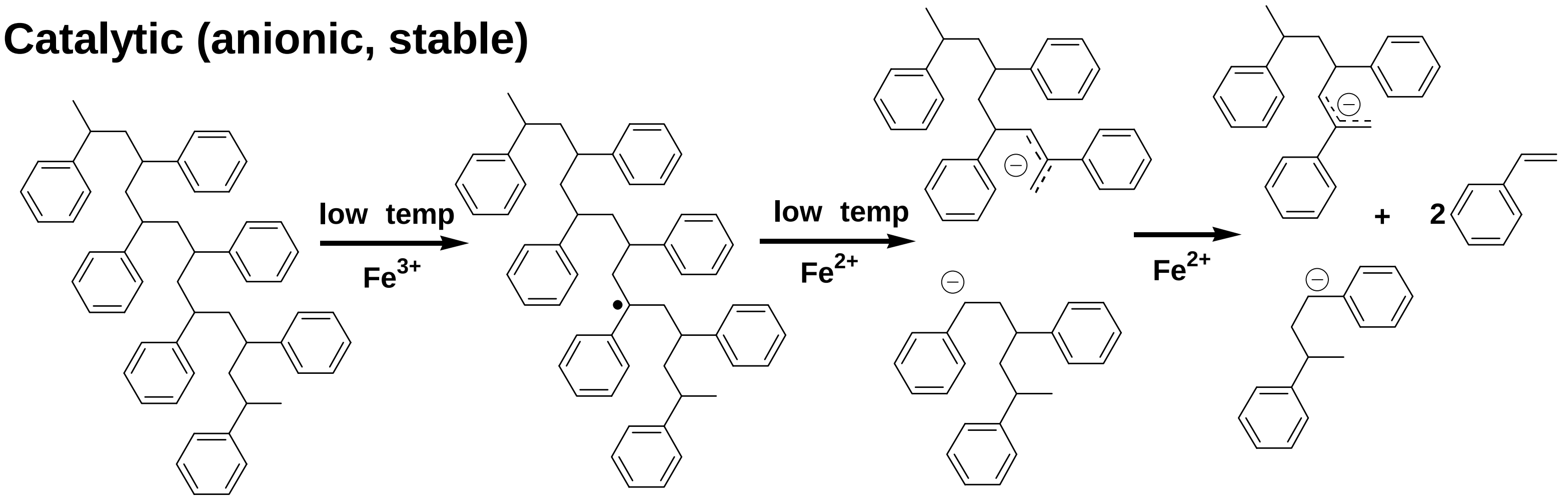
1. Shredder
2. Extruder
3. Pretreatment Vessel
4. Reactor
5. Heat Exchanger
6. Oil Storage
7. Distillation Tower

Selectivity for Catalytic Degradation of PS

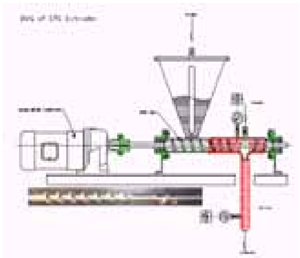
Thermal (radical, unstable)



Catalytic (anionic, stable)



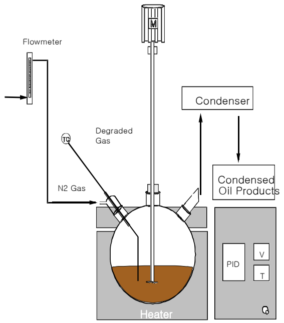
Effect of Melting Temp. for WEPS



Melting temp. (℃)	210	220	250	270	300
Formation of oil (ml/min)	11.2	12.6	14.4	12.95	11.32
Chemical composition of oil (wt %)					
Styrene monomer	67.84	68.21	70.80	69.56	68.56
α−Methyl styrene	2.01	1.78	1.47	1.34	1.18
Toluene	2.90	2.55	1.67	1.52	1.32
Benzene	0.24	0.23	0.16	0.16	0.21
Ethylbenzene	0.87	1.01	0.50	0.42	0.35
Others	26.14	26.22	26.12	27.00	28.38

Note : Reaction Temperature : 380 ℃, KRICT Cat.

Comparison of Catalytic Activites for Various Cats.

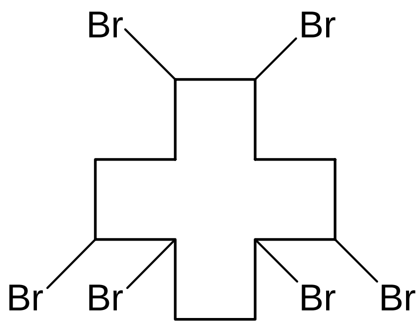


Temp. 380 ℃
WEPS

Catalyst	Thermal	BaO*	MgSO4	BaSO4	KRICT
Formation of oil (ml/min)	15.68	11.82	6.85	17.74	14.41
Product oil (%)	88.0	94.6	84.0	94.5	94.0
Residue (%)	9.3	1.5	13.6	2.6	3.0
Carbon (%)	2.7	3.9	2.4	2.9	2.0
Chemical Composition of Oil (w t %)					
Styrene monomer	58.42	69.25	57.25	59.86	70.8
α−Methyl styrene	1.68	1.07	5.08	4.67	1.47
Toluene	2.01	1.33	2.86	2.00	1.67
Benzene	0.16	0.12	0.23	0.22	0.19
Ethylbenzene	1.94	0.44	2.94	2.37	1.02
Others	35.79	27.79	31.64	30.88	24.85

* Korea Patent 2002−0023472

Degradation of Flame Retardant



1,2,5,6,9,10-Hexabromocyclododecane (HBCD)

- Flame retardant for polystyrene and polyolefin(1963)
- White crystalline solid (Br content of 74.7 wt%)
- Melting point 170-180 ℃
- Bromination of cyclododecatriene, a butadiene trimer

Stoichiometrically

$$C_{12}H_{18}Br_6 \xrightarrow[\Delta]{260\sim280℃} 6HBr + C_{12}H_{12} \xrightarrow{6NaOH} 6NaBr + 6H_2O + C_{12}H_{12}$$

Possible rx. path

$$C_{12}H_{18}Br_6 \xrightarrow[\Delta]{260\sim280℃} 6HBr + C_{12}H_{12}Br \xrightarrow{5NaOH} 5NaBr + 5H_2O + C_{12}H_{12}Br$$

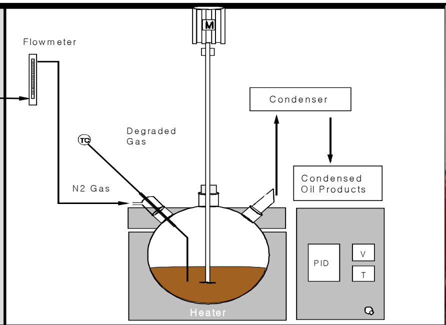
$$C_{12}H_{18}Br_6 \xrightarrow[\Delta]{260\sim280℃} 6HBr + C_{12}H_{12}Br_2 \xrightarrow{4NaOH} 4NaBr + 4H_2O + C_{12}H_{12}Br_2$$

$$C_{12}H_{18}Br_6 \xrightarrow[\Delta]{260\sim280℃} 6HBr + C_{12}H_{12} \xrightarrow{4NaOH} 2HBr + 4NaBr + 4H_2O + C_{12}H_{12}$$

$$C_{12}H_{18}Br_6 \xrightarrow[\Delta]{260\sim280℃} 6HBr + C_{12}H_{12} \xrightarrow{4NaOH} 2HBr + 4NaBr + 4H_2O + C_{12}H_{12}$$

$$\xrightarrow[\Delta]{360℃} C_7H_8 + EB + SM + 2HBr + 4H_2O + C_4H_4$$

Review for Facilities on Various Capacity

Apparatus			
Feed ing Material	GPPS,EPS, WEPS	WEPS	WEPS
Size of Reactor	200 g/batch	6 MT/Y	300 MT/Y
Oil Yield (%)	93	90	90
SM (wt %)	65	65	60

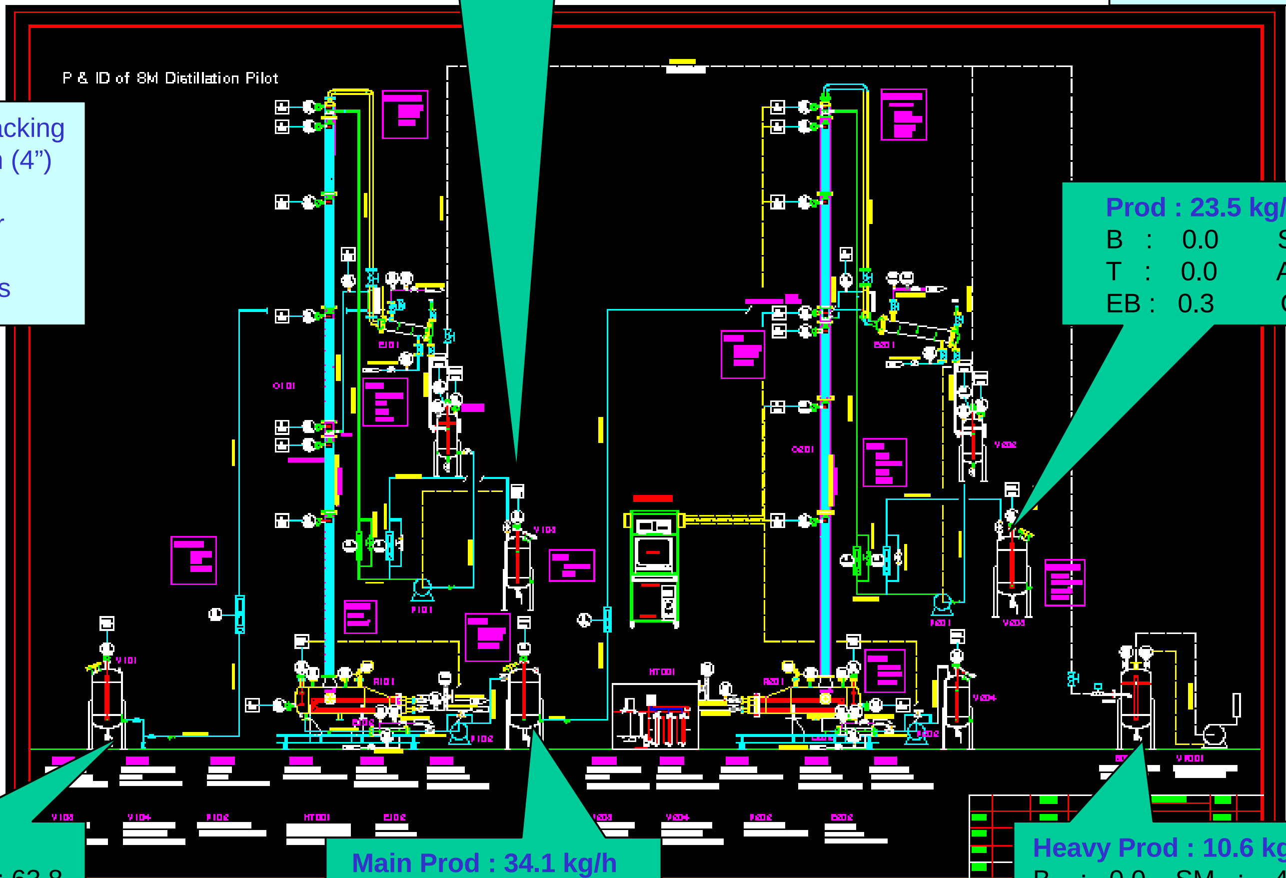
Note: Cat-loading: 1 wt%/WEPS, Temp. 350～400 ℃

Material Balance Using Pilot Distillation Unit

Light Prod : 7.5 kg/h
B : 1.2 SM : 5.8
T : 82.0 AMS : 0.9
EB : 10.1 Oths : 0.0

Column : BX-packing
Diameter : 10 cm (4”)
Hight : 9m
Vacuum : 60 torr
Rf ratio : 10

Column : BX-packing
Diameter : 10 cm (4”)
Hight : 9m
Vacuum : 80 torr
Rf ratio : 20
Recycle : 6 times



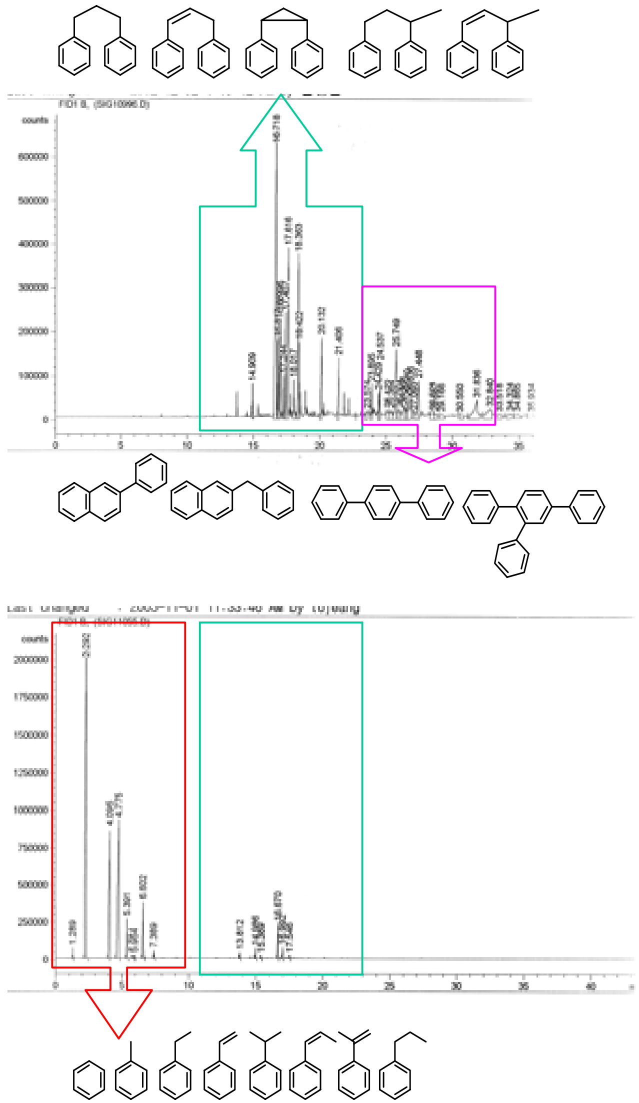
Prod : 23.5 kg/h
B : 0.0 SM : 99.5
T : 0.0 AMS : 0.2
EB : 0.3 Oths : 0.0

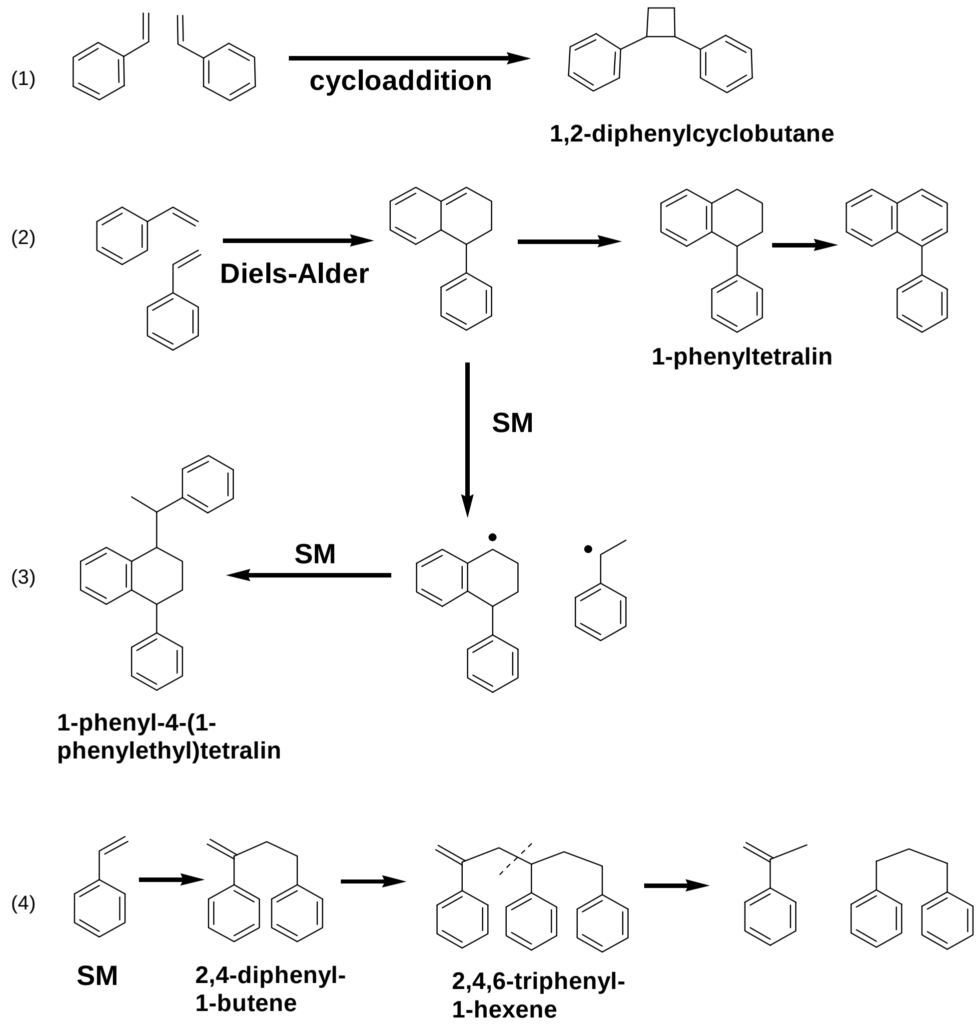
Feed : 41.6 kg/h
B : 0.2 SM : 63.8
T : 10.0 AMS : 5.9
EB : 2.1 Oths : 18.0

Main Prod : 34.1 kg/h
B : 0.0 SM : 70.5
T : 0.0 AMS : 6.8
EB : 0.2 Oths : 22.5

Heavy Prod : 10.6 kg/h
B : 0.0 SM : 4.8
T : 0.0 AMS : 20.1
EB : 0.1 Oths : 75.0

Formation and Analysis of Distillation Residue(Dimer, Trimer)





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Re-pyrolysis of Dimers under 3 atm

Run No.	Temp	Feed	Oil	Composition of oil (Wt. %)					
	°C	g	g	BEN	TOL	EB	SM	AMS	Others
1	360	30.0	4.9	0.2	38.0	1.0	38.5	8.3	13.91
			9.9	0.3	41.0	0.0	49.5	9.1	0.1
2	360	30.0	20	0.3	42.2	0.0	35.7	9.4	12.46

Note : distillation residue including dimers

Comparison of Virgin SM and Recovery SM on Preparation of EPS

Test for Application using Recovered SM monomer

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Conclusions

1. Waste materials containing EPS, FEPS, FREPS etc were changed to pyrolysis feed through solubilization and shredding.

2. Operation conditions for each continuous process were optimized such as melting temp.,pyrolysis temp., catalyst loading amount and separation conditions etc.

3. Alkali promoted catalysts were screened for selective pyrolysis of WEPS,WFEPS,WFREPS.