Regular Fugitive Emission Characteristics of HFC-134a from Mobile Air Conditioners (MACs) of Korea-Made Passenger Vehicles in Korea

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Contents

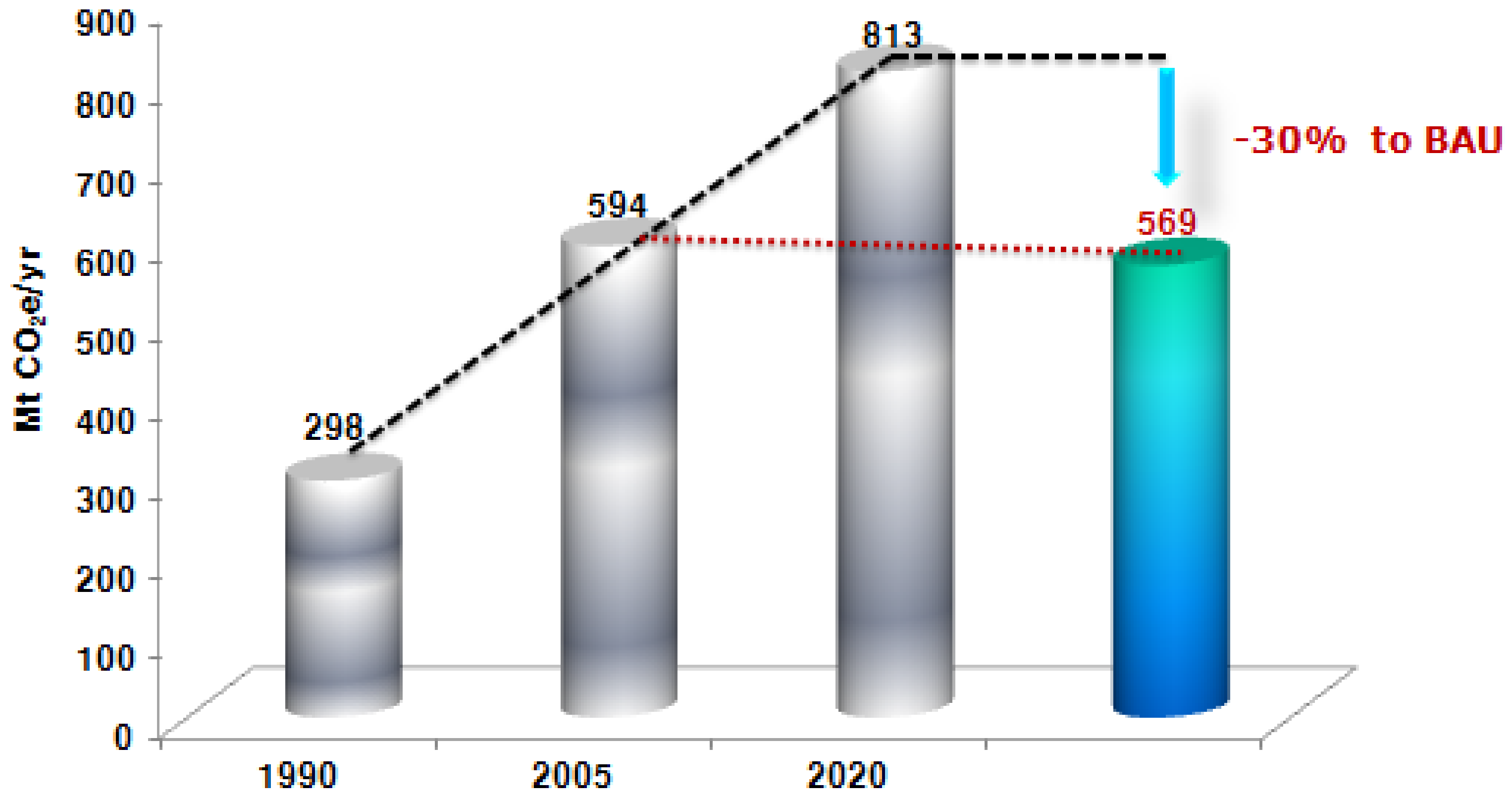
1. Backgrounds

GHG emission status of Korea

Korea

Sharp increase in CO_2 emissions for the past 15 years due to manufacturing-based industrial development (99% increase from 1990 to 2005, Ranked 1st among OECD countries in terms of rate of increase)

National GHG reduction target



How can we achieve the reduction target?

- **2008** — **Low Carbon, Green Growth** was proposed as a core of Republic's new vision
- **2009** — **GHG reduction target was announced:** 30% reduction in 2020 BAU(about 245 Mt CO_2e)
- **2009** — **Framework Act on low carbon, green growth**
- **2010** — **GHG Target Management Scheme**
- **2015** — **Emission Trading Scheme**

Demand for Accurate Inventory

- **GHG Target Management System and Emission Trading System require high accuracy of inventory;**
- **Korea is now reconstructing inventories of all sectors;**
- **HFC is one of the target GHGs for inventory reconstruction project.**
  - Two years project (2011. 7. ~ 2013. 8.) was carried out for developing F-Gas Inventory.

Why HFC inventory is in high priority?

- **High Global Warming Potential of HFCs demands accuracies of its emission data;**
  - Minor errors made during the courses of inventory preparation can allow significant deviation of inventory
- **There are various emission sources of HFCs and difficulties in collecting activity data;**
- **We did not have country-specific and/or plant-specific EFs for HFCs.**

Refrigerant of MAC (Mobile Air Conditioner)

History of Vehicle Refrigerant

'89 — **Montreal Protocol : Regulation of CFC and HCFCs Use**

"R-12 was major refrigerant"

'96 — **Conversion to R-134a for New Cars**

'05 — **Kyoto Protocol : Regulation of GHG Emission**

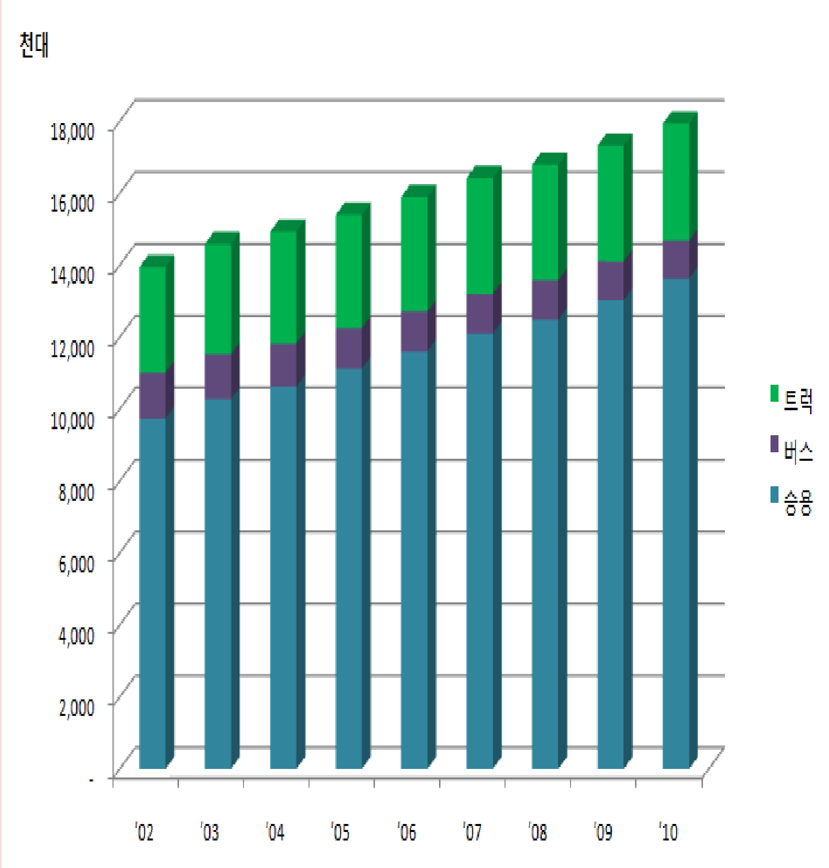
'11 — **Conversion to R-1234yf for New Car**

Characteristics of Refrigerants

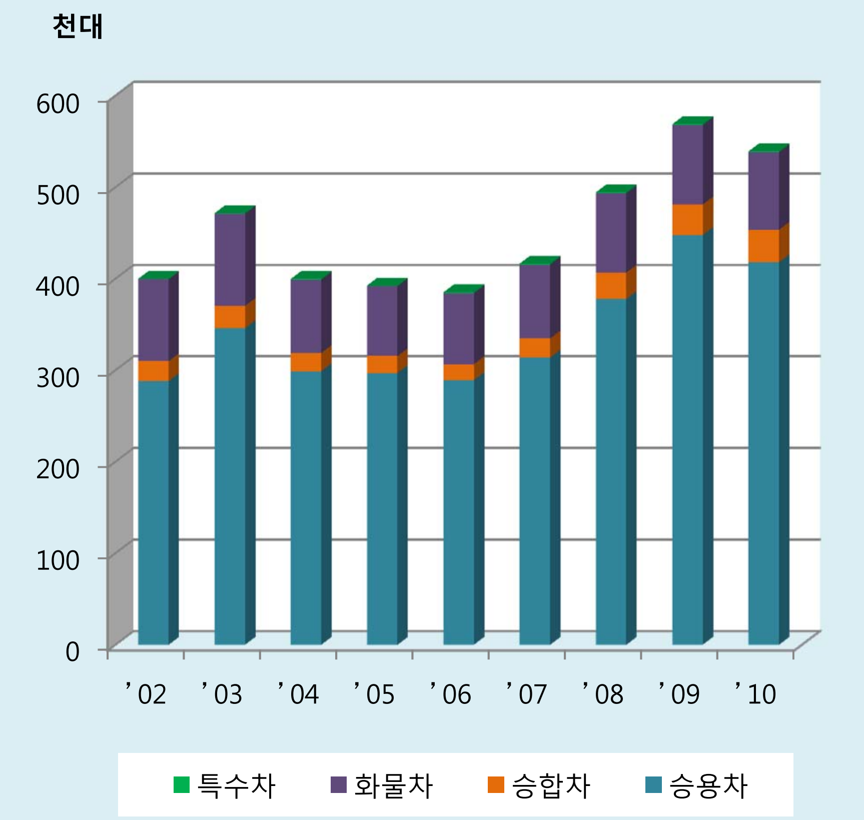
Item	R-12	R-134a	R-1234yf
Formula	CCl_2F_2	CH_2FCF_3	$C_3H_2F_4$
Toxicity	No	No	No
Flammability	No	No	A little
ODP	1.0	0	0
GWP	8,500	1,300	4

Statistics for Vehicle in Korea

Registration Status by Vehicle Type



Statistics for Scrap Vehicles



Previous Studies

- **Regular Emission**
  - Siegl et al. (2002) : 25.4 g/yr per vehicle at a stationary mode
  - Stemmler (2004) : 122.6 g/yr per vehicle at a dynamic mode
  - Schwarz (2005) : 52.6 g/yr per vehicle (EF = 6.9%/yr)
  - Japan (2009) : EF = 5.2%/yr
- **Total Emissions including regular and irregular emission**
  - IPCC (2006) : EF = 10~20%/yr

Research Objectives

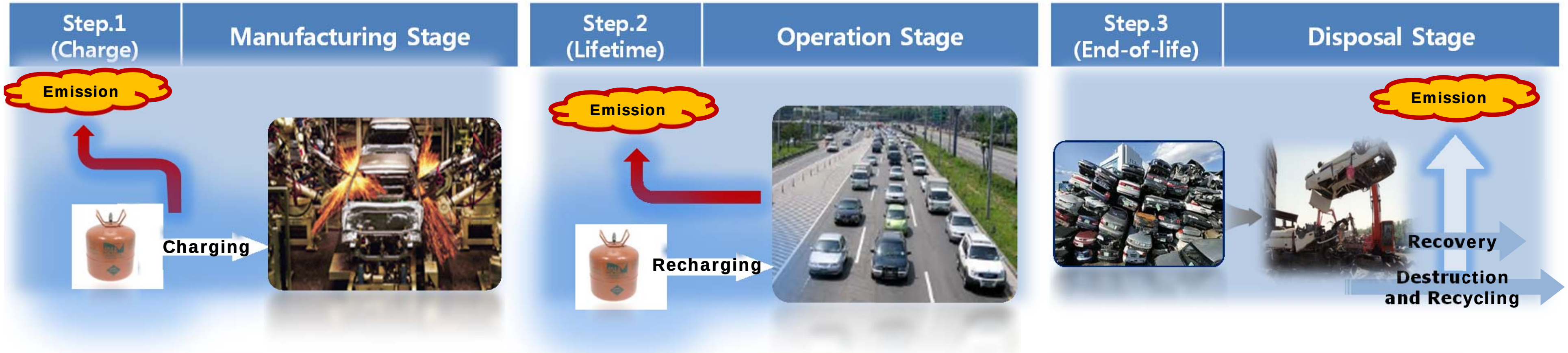
- **This research attempts to**
  - Develop the emission model of HFC-134a from MAC of passenger vehicles to simulate its regular emission kinetics;
  - Develop country-specific emission factors of HFC-134a from MAC of passenger vehicles at use-phase and disposal-phase;
  - Estimate the fugitive emission inventory of HFC-134a from MAC of passenger vehicles.

2. Theoretical

Methodologies of 2006 IPCC Guidelines

Tier			Description
Tier 1	Tier 1a	Emission Factor Approach at the application level	• **Activity Data: Net Consumption** Net Consumption = Production + Imports – Exports - Destruction • **Annual Emission = Net Consumption • Composite EF**
	Tier 1b	Mass Balance Approach at the application level	• Emissions = Annual Sales of New Chemical – (Total Charge of New Equipment – Original Total Charge of Retiring Equipment)
Tier 2	Tier 2a	Emission Factor Approach at the **sub-application** level	$E_{total,t} = E_{containers,t} + E_{charge,t} + E_{lifetime,t} + E_{end-of-life,t}$ ※ $E_{lifetime,t} = B_t \times \frac{x}{100}$; B_t stands for HFC banked in existing equipment at year t and x does for EF
	Tier 2b	Mass Balance Approach at the sub-application level	• Emissions = Annual Sales of New Refrigerant – Total Charge of New Equipment + Original Total Charge of Retiring Equipment – Amount of intentional destruction

Emission Points of Refrigerants(HFC-134a)



- **Manufacturing Stage :**
  - HFC-134a may be emitted accidentally during its injection to MAC
- **Operation Stage :**
  - HFC-134a may be emitted during the operation of MAC through the construction materials and connection points
- **Disposal Stage :**
  - HFC-134a remained in MAC will be emitted eventually

Two Questions for Emission Factor of MAC

- **Are the Emission Factors constant over time?**
- **Is the previous estimation method right?**
  - EF = (Original Charged Amount of HFC-134a into MAC – Remaining Amount of HFC-134a in Retiring MAC)/Operating Years

Development of Basic Concepts

Fugitive Emission of Refrigerant from Vehicle is expressed as a function of 1) Car Age and 2) Operation Time of MAC

*CAR AGE REPRESENTS THE DEGRADATION DEGREE OF MAC AND FUGITIVE EMISSIONS OF REFRIGERANT CAN BE MADE THROUGH THE DEGRADED CONNECTION PARTS OF MAC

*FUGITIVE EMISSIONS OF REFRIGERANT INCREASES WITH INCREASING OPERATION TIME OF MAC. HOWEVER, IT IS IMPOSSIBLE TO DETERMINE THE OPERATION TIME OF MAC FOR INDIVIDUAL CARS. INSTEAD WE DECIDED TO USE CAR AGE AND MILEAGE.

WE DEVELOP TWO MODELS BASED ON 1) CAR AGE AND 2) MILEAGE

First-order Emission Model (FEM)

Assumptions

- **Emission Rate of Refrigerant is proportional to the residual amount of refrigerant;**
- **Emission rate constant is unvaried with car age.**

Fugitive Kinetic Equation for Refrigerant

$$\frac{dM_e}{dt} = -\varepsilon \cdot M_e$$

where M_e **: Residual amount at year *t* (g)**

ε **: Apparent emission rate constant(yr^{-1})**

First-order Emission Model (FEM)

Apparent Emission Rate Constant

$$\varepsilon = \frac{\ln\left(M_e / M_0 \right)}{-t}$$

1. Get information on original charged or recharging amount : M_0
2. Determine the residual amount of refrigerant : M_e
3. Determine the duration time after refrigerant charging (original or recharge)

Residual Amount as a function of time

- $M_e = M_0 \cdot \exp(-\varepsilon \cdot t)$ where M_0 is the original charged amount or recharged amount(g)

First-order Emission Model (FEM)

Total Emission Amount at year *t*

- **Difference in residual amount between *(t-1)* and *t* year**

$$EA(t) = M_e(t-1) - M_e(t) = M_0 \cdot [exp\{-\varepsilon \cdot (t-1)\} - \exp(-\varepsilon \cdot t)]$$

where *EA* represents Emission Amount(g) during one year between year *(t-1)* and *t*.

Emission Factor(Annual Emission Rate)

$$x(\%) = \frac{EA(t)}{M_e(t-1)} \times 100 = \{1 - \exp(-\varepsilon)\}$$

where EA(g) is the Emission Amount during the one year from year *(t-1)* and *t* and *x*(%) is Emission Factor(annual emission rate)

3. Experimental

Recovering Refrigerants

◆ **Potable Recover: Yellow Jacket XLT / 95763, USA**

Specification for recover	
Upper limit of weigh	50 kg
Minimum unit	2 g
Precision	± 0.5 %
Suction pressure	0.50 bar

Disposal Stage : Measurement Practices

Analyses of Refrigerant Compositions

Condition

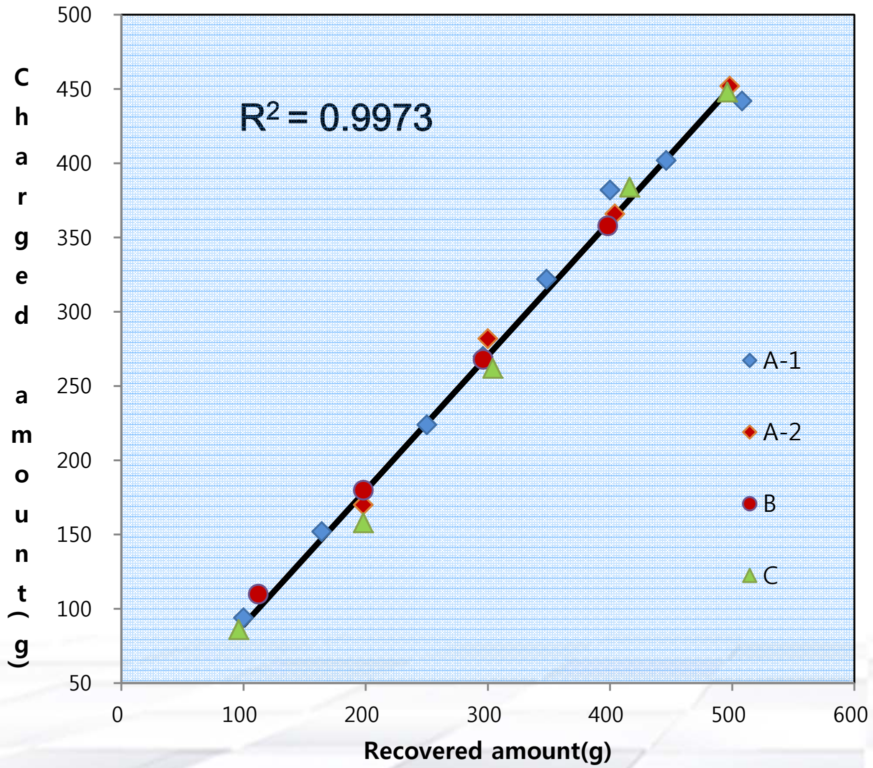
Item	Condition of GC-MSD
Inlet	220 ℃, Split ratio 100 : 1
Column	DB-624 (60 m X 0.25 mm X 1.4 um)
Flow	He , 1 mL/min
Oven	40 ℃ (5 min) → 10 ℃/min → 80 ℃ → 250 ℃
Scan range	45 ~ 300 m/z (EI mode)
Injection volume	0.5mL
Tedlar Bag	1L(PVF Film)

4. Results and Discussion

4.1. Emission Characteristics

Calibration Results

- **There may be Limiting Recovery Performance of recover used here and average recovery rate was 90.6±3.7 % → Calibration was proposed**



$$M_r = 1.0872 \times M_m + 6.4098$$

where M_r stands for calibrated amount and M_m for recovered amount (reading value) offered by the recover

Fugitive Emission Results at Use-phase

No.	Type	Model	Mileage (km)	Original Charged Amount(g)	Recovered Amount (g)	Residual Amount(g)	Residual Rate(%)	Emission Constant (%/yr)	Annual Emission Rate(%/yr)	Average of Emission Rate (%/yr)
1	Large	2004	23,140	550	468	518.39	94.25	0.88	**0.87**	**4.6±0.8%***
2		2009	98,498	550	412	455.6	82.8	5.79	**5.6**	
3		2004	59,408	650	410	453.4	69.7	4.46	**4.4**	
4		2002	166,322	700	456	504.9	72.1	3.35	**3.3**	
5		2005	109,987	750	498	552.0	73.6	4.43	**4.3**	
6	Medium	2011	15,727	550	460	509.42	92.62	0.04	**4.28**	**5.2±0.9%***
7		2007	108,750	550	288	316.56	57.56	11.84	**0.11**	
8		2003	97,458	550	372	410.75	74.68	3.50	**3.44**	
9		2008	65,459	780	576	639.5	82.0	0.05	**5.3**	
10		2006	89,654	500	354	390.6	78.1	3.95	**3.9**	
11	Small	2003	69,155	700	292	321.05	45.86	8.66	**8.30**	**5.0±1.2%***
12		2007	25,094	500	366	404.02	80.80	5.12	**4.99**	
13		2010	20,359	500	444	491.48	98.30	1.03	**1.03**	
14		2006	36,404	550	360	397.29	72.24	5.66	**5.50**	
15		2009	57,948	480	402	444.39	92.58	3.19	**3.14**	
16	Mini	2002	115,370	550	290	318.80	57.96	5.79	**5.63**	**5.6±1.2%***
17		2010	51,866	450	316	347.96	77.32	4.47	**4.37**	
18		2009	28,708	450	294	323.29	71.84	11.34	**10.72**	
19		2002	76,247	550	282	309.83	56.33	6.04	**5.86**	
20		2007	84,658	450	288	316.6	70.3	5.21	**5.1**	

*** : 95% confidential interval**

Summary of fugitive emission characteristics of HFC-134a from MAC of passenger vehicle at use-phase

Vehicle type	Original charged amount(g)	Average operating time(yr)	Mileage (1,000km)	Average residual rate (%)	Apparent fugitive emission constant (yr^{-1})	Emission Factor (%/yr)	Emissions per kilometer (mg/km)
Mini (n=8)	512.5±43.3	9.5±2.5	94.9±29.0	58.9±8.5	0.0579±0.0126	5.6±1.2	2.36±0.60
Small (n=14)	616.4±51.9	9.2±1.8	125.1±28.3	65.4±7.3	0.0512±0.0125	5.0±1.2	1.88±0.40
Medium (n=18)	657.6±47.1	8.5±1.8	119.7±26.4	65.2±8.1	0.0541±0.0092	5.2±0.9	2.03±0.36
Large (n=7)	712.9±102.3	7.5±2.4	110.4±30.2	71.7±7.4	0.0468±0.0087	4.6±0.8	1.96±0.73
Average	**624.5±31.6**	**8.7±0.9**	**114.4±13.4**	**65.4±3.9**	**0.0526±0.0051**	**5.1±0.5**	**2.02±0.21**

Emission rates and quantities of HFC-134a from MAC at the use-phase in 2011

Type	2011 registration number	Emission rate per car (g/yr)	Total emission (tCO_2-eq)
Mini	1,234,373	21.0	33,662
Small	2,008,689	23.2	60,621
Medium	5,495,505	25.7	183,643
Large	2,042,714	25.2	66,893
Sum	10,781,281	-	344,819
Weighted average	-	24.6	-

Emission Factors of Vehicle Types during Operation Stage

Vehicle Type	Emission Factor(%/yr)	IPCC Default Value(%/yr)
Mini Size	5.6	10 ~20
Small Size	5.0	
Medium Size	5.2	
Large Size	4.6	

- **HFCs Emission Amount using country-specific(CS) EFs in 2011 is 344,819 tCO_2 eq, whereas the IPCC default EFs allows 539,609 tCO_2 -eq higher(56%) than the emission amounts derived by the CS EFs**

Overestimation if we adopt the IPCC default value

Residual Amounts of Refrigerant in Scrap Vehicles

Type	Model	Mileage(km)	RA(g)	CA(g)	Residual Rate(%)	Average Residual Rate(%)
Mini	'05. 8	244,292	448.00	495.97	**90.2**	51.4±2.4%(n=91)
	'94. 7	130,867	430.00	475.79	**73.2**	
	'97. 10	172,464	380.00	419.72	**76.3**	
	'96. 3	177,142	317.00	349.08	**69.8**	
	'97. 8	150,370	252.00	27.19	**50.2**	
Small	'03. 5	193,380	382.00	421.96	**64.9**	51.2±1.9%(n=157)
	'97. 10	148,518	482.00	534.09	**73.2**	
	'00. 2	118,986	360.00	397.29	**55.2**	
	'98. 8	152,464	428.00	473.54	**63.1**	
	'01. 3	151,013	369.00	407.39	**71.5**	
Medium	'00. 9	82,118	460.00	509.42	**69.8**	55.2±2.0%(n=106)
	'04. 1	110,008	461.00	510.55	**65.5**	
	'99. 5	95,815	480.00	531.85	**72.9**	
	'05. 7	90,708	334.00	38.14	**56.6**	
	'06. 1	141,792	428.00	473.54	**72.9**	
Large	'01. 5	174,312	324.00	356.93	**47.6**	58.4±3.4*%(n=39)
	'03. 2	174,126	412.00	455.60	**44.7**	
	'99. 6	194,792	391.00	432.05	**63.5**	
	'97. 6	212,432	441.00	488.12	**54.2**	
	'00. 4	266,442	511.00	566.61	**55.6**	

* : 95% confidential interval

Average : 55.6±1.1%

Residual rates of HFC-134a in MACs of scrap passenger vehicles

Vehicle type	Original Charged Amount (g)	Average age (yr)	Average Residual Rate (%)
Mini (n=91)	552.8±5.6	12.2±0.3	51.4±2.4
Small (n=157)	673.2±15.0	12.7±0.6	51.2±1.9
Medium (n=106)	680.0±14.9	11.7±0.7	55.2±2.0
Large (n=39)	833.8±41.7	12.8±0.8	58.4±3.4
Average	689.5±4.2	12.4±0.2	55.6±1.1

Emission Amount from Scrap Vehicles in 2011

Vehicle Type	Scrap Quantities in 2011	Emission per Vehicle	Emission Amount (tCO_2 eq)
Mini Size	45,959	284.1	16,974
Small Size	382,351	344.7	171,335
Medium Size	193,905	375.4	94,630
Large Size	24,523	486.9	15,522
Total	**646,739**	**383.4**	**322,348**

Total Emission Amount from Passenger Vehicles in 2011

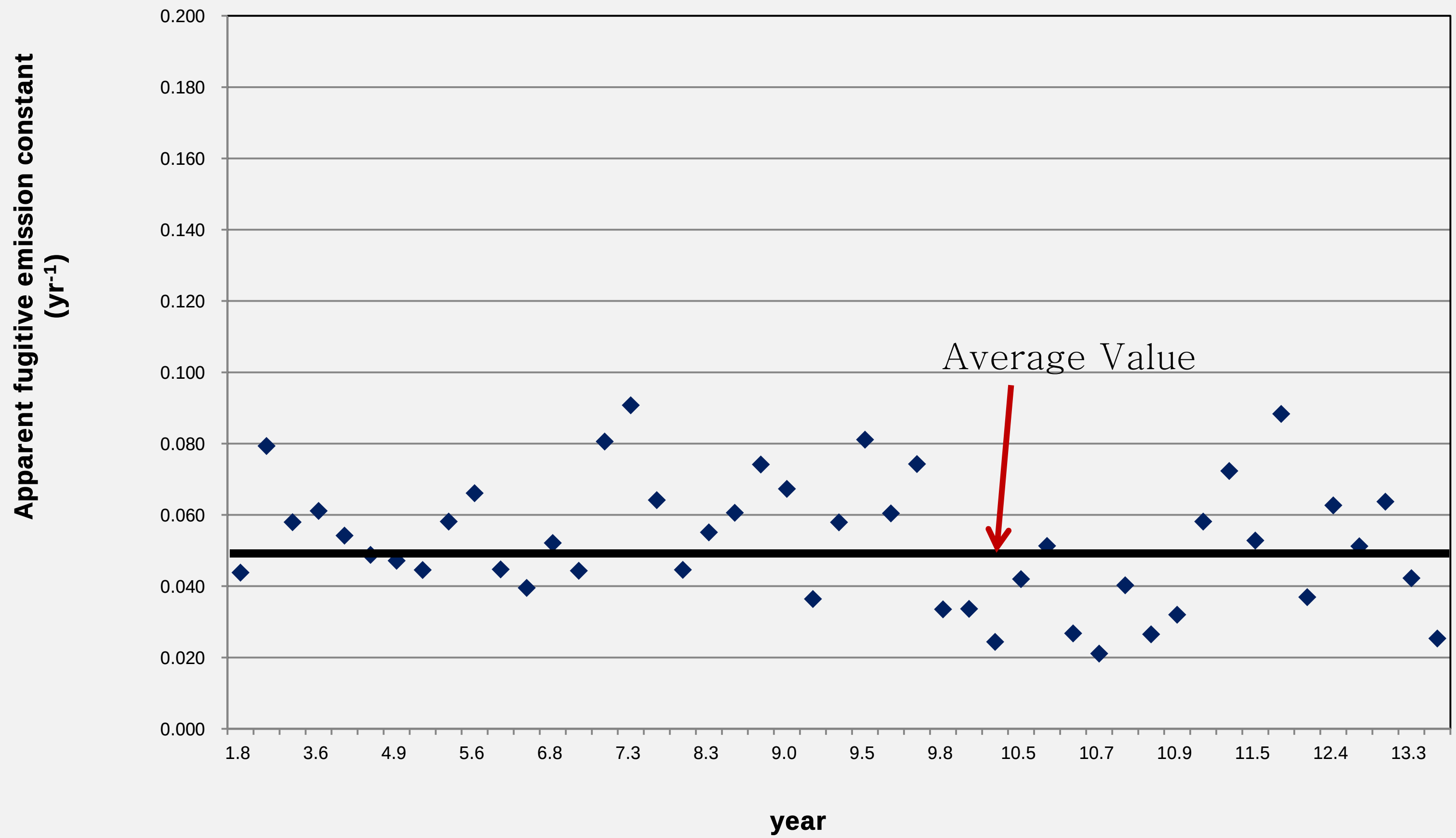
Vehicle Type	Use-phase (tCO_2 eq)	Disposal-phase (tCO_2 eq)	Sum
Mini Size	33,662	16,974	50,636
Small Size	60,621	171,335	231,956
Medium Size	183,643	94,630	278,273
Large Size	66,893	15,522	82,415
Total	**344,819**	**322,348**	**667,167**

4.2. Verification of Emission Model

Verification Methodologies

- Checking the **consistency of apparent fugitive emission constant** with vehicle age
- Comparing the **residual rates** of scrap passenger vehicles measured here with **those predicted by using the apparent fugitive emission constant derived from use-phase analyses**

Consistency of Apparent Emission Constant with vehicle age



Comparison of Experimental Residual Rates with Theoretical Ones

Type	Measured residual rate (%)	Predicted residual rate (%)	Deviation* (%)
Mini	51.4	49.3	-4.1
Small	51.2	52.3	+2.2
Medium	55.2	53.2	-3.7
Large	58.4	54.8	-6.2
Average**	-	-	**4.0**

*: (Predicted residual rate – Measured residual rate)/Measured residual rate X 100
**: Average of absolute values of deviation

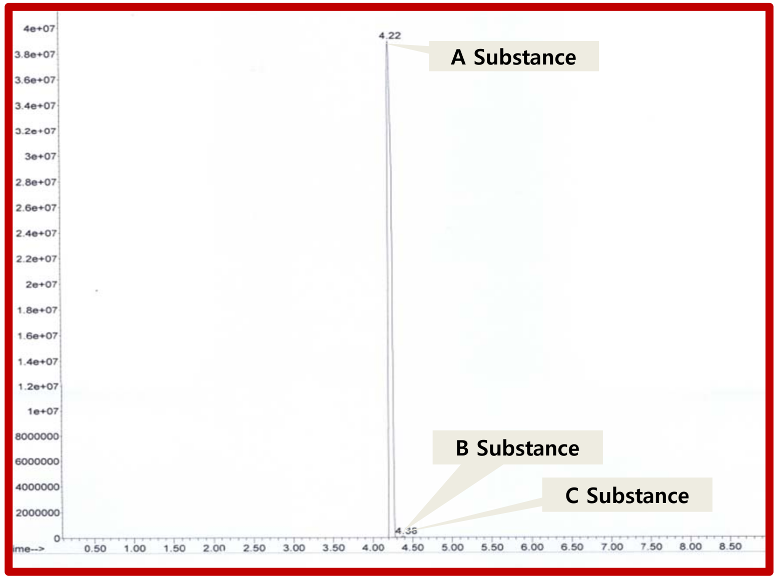
4.2. Chemical characterization of refrigerant in scrap vehicles

Necessity for Chemical Characterization

- **Korean Waste Act proposed that over 99% purity of original refrigerant should be maintained for reuse.**
- **Other refrigerants than HFC-134a may be injected during the recharging process.**
  - Small-size repair shop may replace with cheaper refrigerant (e.g. CFCs) during the course of recharging processes

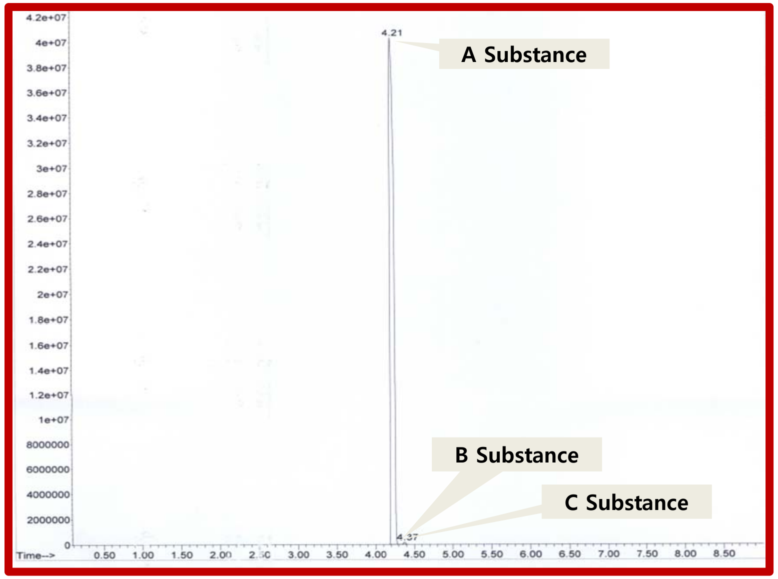
Chemical Characterization of New Refrigerant(HFC-134a)

Gas-phase HFC-134a



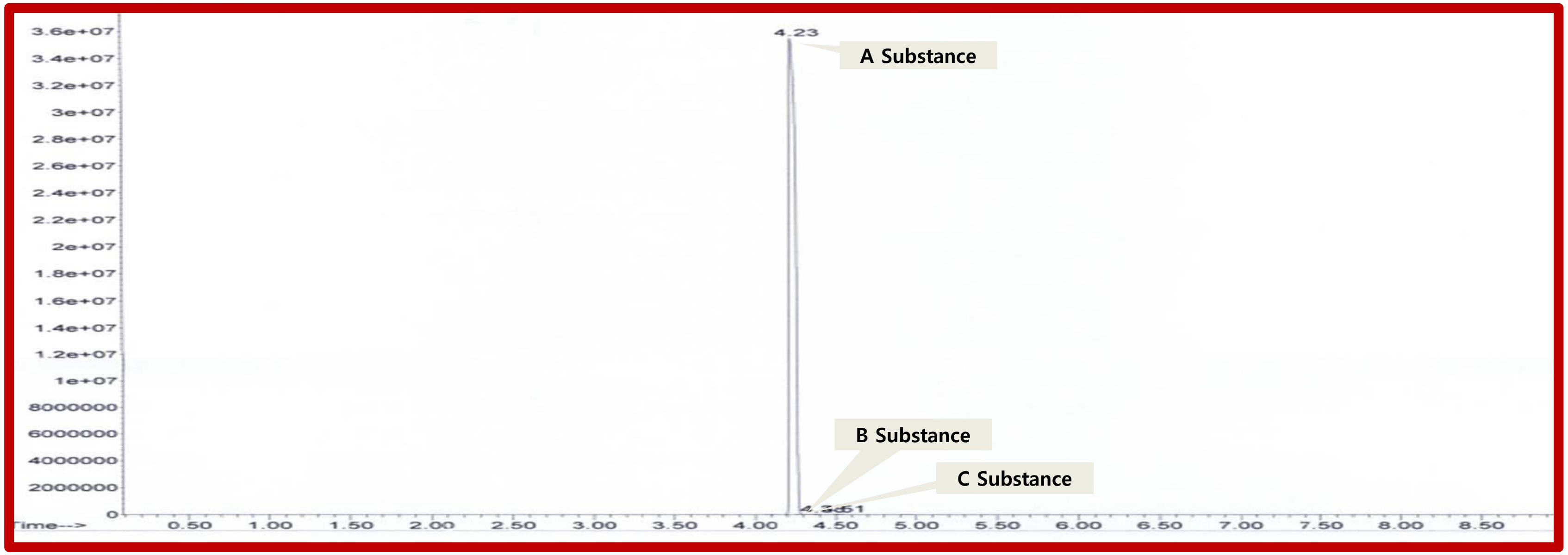
Po.	Ret Time (min)	Area (%)	Compound
A	4.225	99.850	1,1,1,2-Tetrafluoroethane
B	4.378	0.150	1,1,2,2-Tetrafluoroethane
C	4.509	Negligible	Dichlorodifluoro-methane(R-12)

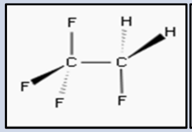
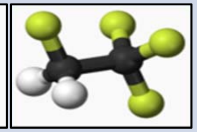
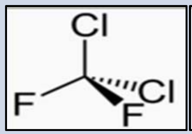
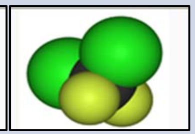
Liquid-phase HFC-134a



Po.	Ret Time (min)	Area (%)	Compound
A	4..213	99.788	1,1,1,2-Tetrafluoroethane
B	4.372	0.212	1,1,2,2-Tetrafluoroethane
C	4.511	Negligible	Dichlorodifluoro-methane(R-12)

Chemical Characterization of Refrigerant recovered from scrap vehicle



	Ret Time(min)	Area (%)	IUPAC name	Compound
A	4.231	99.894	1,1,1,2-Tetrafluoroethane	 
B	4.378	0.049	1,1,2,2-Tetrafluoroethane	
C	4.513	0.06	Dichlorodifluoromethane	 

3. Conclusions and Suggestions

Conclusions and Suggestions

- **First-order Emission model (FOM) and apparent fugitive emission constants are reasonable appropriate for estimating the emission rates of Korea-made vehicles operated in Korea ;**
  - Average apparent fugitive emission constant : **0.0526±0.0024 yr^{-1}**
  - Average emission factor : **5.1±0.5 %/yr**
  - Average age at disposal : **12.4 years**
  - Average residual rate of scrap passenger vehicle : **55.6±1.1 %**
  - Annual emission rate per passenger vehicle
    - Use-phase : **24.6 g**
    - Disposal-phase : **383.4 g**
    - Life Cycle Emission(12.4 years) : **688.4 g**

Conclusions and Suggestions

- **This research reported the fugitive emission amount of HFC-134a from passenger cars to be 667,167 tCO_2 eq, whereas the official amount reported by Korean Government to be 1,398,723 tCO_2 eq**
  - Reason for difference : Application of different emission factors
    - This research : EFs developed by *in situ* measurements
    - Official data : IPCC default EFs

It is essential to adopt car-specific EFs developed here to estimate the emission amount of HFC-134a from passenger vehicles

Conclusions and Suggestions

- This research demonstrates that the chemical compositions of refrigerant were rarely varied to compare with those of new one

It is possible to reuse the refrigerant recovered from scrap vehicles

Publications

- 2014; Journal of Industrial Engineering and Chemistry, In Press;
- Three Papers(2 papers in 2012, one paper in 2013) in Journal of Korea Society of Waste Management;
- 2013; in Journal of Environmental Science International

Thanks

Question ?

Answer !