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Waste Refrigerants Flows: A Case Study of Domestic Refrigeration in Ukraine

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Industrialization and advancement of living standards are increased rapidly driving the refrigerants market. In many countries, old-type refrigerants (including those not accepted in new equipment) are still in wide use. For domestic refrigeration, R134a and R600a are mainly used, their share is around 26% of total refrigerants amount. The purpose of this research is to assess the recovery potential and contribution of refrigerants to global warming through the calculation of their residual volumes in old equipment using household fridges as a case study. A comprehensive analysis of old household fridges in Ukraine was conducted: 42 household fridges (in use) were studied. Apart of R600a and R134a refrigerants as the most widely used, some very old household fridges contain R12 refrigerant. Generally, refrigerant content ranges from 0.032 to 0.175 kg per item with average value 0.075 kg. The average R134a content is higher comparing to R600a: 0.115 and 0.058 kg per item, respectively. The residual weight of R134a and R600a refrigerants in one fridge was estimated at 0.058 and 0.029 kg, respectively. Taking into account the number of waste household fridges, the average annual amount of residual R600a refrigerant is higher (1.4 tonnes) comparing to R134a (about 1 tonne). Total refrigerant recovery potential for domestic refrigeration was estimated at 2 tonnes per year (counting 80% recycling rate). Due to the lack of separate collection of waste electrical and electronic equipment in Ukraine, both the residual refrigerant and its loss contribute to greenhouse gas emission, which was estimated at about 2652 tonnes of CO_2-equivalent/year with R134a refrigerant as the main contributor. This data can be used for improvement of waste household fridges and residual refrigerant management.

Keywords: refrigerant, household fridges, global warming, residual refrigerant, refrigerant recovery.

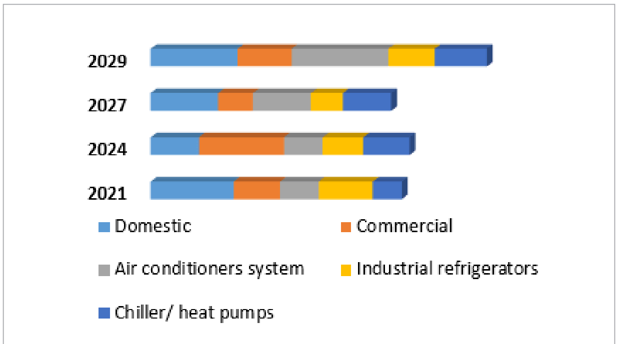
Introduction

Industrialization and raise of living standards rapidly drive the refrigerants market (*Fig. 1*). Refrigerants use is constantly growing with higher utilization in developing countries (Booten et al., 2020). Asia-Pacific region dominates the market of refrigerants due to the high demand and a vast number of users in this region.

Developing countries such as China, India, and Indonesia are contributing more to this market because of the increase in the living standards and disposable income.

Previous refrigerants were known to cause ozone depletion, while new refrigerants are responsible for global warming due to a large amount of carbon emissions during the life cycle of their production and use (Wang et al., 2021). European regulation has banned the use of refrigerants with global warming potential (GWP) values higher than 150 (Maiorino et al., 2020). Therefore, modern refrigerants must be of both low-global warming potential a zero-ozone depletion potential (Vuppaladadiyam et al., 2022). Refrigerant applications are as follows: air conditioning systems, thermal management systems, incl. cooling battery packs and onboard computers in hybrid vehicles, foam production, aerosols, fire suppression, and chemical solvents. Another new growing application is increasing number of data centres demanding temperature control for server rooms. These are vapor compression systems that primarily use fluorocarbon refrigerants. Poor servicing procedures and the absence of refrigerant recovery and recycling often lead to the emission of a significant amount of the refrigerants directly into the atmosphere (UNEP, 1999).

Fig. 1. *Refrigerant world market in near future (Source: Maximize Market Research Pvt. Ltd.)*



It is known that ozone-depleting R12 refrigerant (dichlorodifluoromethane) and other chlorofluorocarbons had been replaced by hydrofluorocarbons like R134a (1,1,1,2-tetrafluoroethane) that, in turn, were found to have high greenhouse effect (global warming potential of 1 kg of R134a is equivalent to 1300 kg of carbon dioxide (Wang et al., 2021)). However, there are alternatives to R134a: R1234yf (hydrofluoroolefine) and R744 (carbon dioxide) have much lower global warming potential. According to Yadav et al. (2022), R290 (propane) and R1234yf (2,3,3,3-tetrafluoropropene) refrigerants are found to be promising alternatives to be used as 21st-century refrigerants. But hydrofluoroolefins have short atmospheric life and get decomposed in the atmosphere and form tri-fluoro-acetic acid, which is harmful to the aquatic environment (Mohanraj and Abraham, 2020).

There are many old-fashioned systems with refrigerants of previous generations. Mostly, new refrigerants cannot be used where originally another refrigerant was pumped in. For example, R744 operates at much higher pressure comparing to other refrigerants; pure hydrocarbon refrigerants cannot be used in R134a systems because of mismatches at volumetric cooling capacity and operating pressures (Kumma and Kruthiventi, 2023).

Yearly use of refrigerants in vapor compression equipment for refrigeration is estimated at 389,000 tonnes (Booten et al., 2020) with R22 (chlorodifluoromethane) as a main refrigerant (the share is over 50%), though R22 (as ozone-depleting) has to be totally replaced by 2040. Other most widely used refrigerants are R404a (blended R125, R143a and R134a), R134a, R410a (blended R32 and R125). Similar data were found for heating, ventilation, and air conditioning (HVAC): R410a and R22 cover 85% (Booten et al., 2020) of refrigerants market. Also, ultralow-temperature refrigeration commonly uses refrigerants with very high GWP values, such as R23 (trifluoromethane) and R508B (perfluorocarbon blend) (Mota-Babiloni et al., 2020).

Besides, there are constant leakages of refrigerants. For example, leakage from automobile air-conditioning system during car recycling was estimated up to 450 g per one car (Wang et al., 2021). Additionally, there are so many small (and short-time) sources of hydrofluorocarbons emissions (Palandre et al., 2003) that one cannot take into account all of them while focusing on the largest sources like air-conditioning and refrigerating equipment. The halocarbon refrigerants released in disposal facilities are estimated to be more than 20% (Lee et al., 2017). Also, in the case of a compressor burnout, the remaining refrigerant can be recovered but it is contaminated and non-recyclable (UNEP, 1999).

Forti et al. (2020) have found about 98 million tonnes of greenhouse gases released into the atmosphere during the recycling of undocumented refrigerators and air conditioners (40% in Europe and 82.6% in the rest of the world). At the same time, greenhouse gas emission due to improper processing of waste refrigerants from air conditioners exceeds the emission of waste refrigerants from refrigeration equipment (73% versus 27% in 2019). This is because refrigerants with high global warming potential were used before 1994 (e.g., R11 and R12) and until 2017 (R134a and R22). Since then, these refrigerants have been replaced by others with much lower GWP (such as R152a and R1234yf). However, the reduction in greenhouse gas emissions due to refrigerants replacement will be evident only in the next decades, when new products placed on the market will become a waste.

Today, more supermarkets use CO_2 and NH_3 as refrigerants in their refrigerated showcases. In smaller stores, split-type refrigerated cabinets typically use CO_2, while monoblock refrigeration units mostly use propane (R290) (Ciconkov, 2018).

For domestic refrigeration, R134a and R600a (isobutane) are mainly used. According to Straub (2018), since the beginning of the 1990s it is common in Europe to use R600a as a refrigerant in household appliances. Also, Belman-Flores et al. (2022) have found new R513a refrigerant (hydrofluoroolefin and hydrofluorocarbon refrigerant blend) more energy-saving and with less global warming impact. Besides, Sruthi and Kumar (2018) consider the use of natural refrigerants like CO_2, NH_3 and hydrocarbons such as R290, R600, R600a and blends of hydrocarbons for domestic refrigeration as possible solution to address the issue of ozone depletion and global warming. On the other hand, R404a (blended R125, R143a and R134a) and R22 are additionally used for commercial refrigeration (R22 in developing countries), and R717 (ammonia) for industrial refrigeration (Booten et al., 2020). The share of R134a and R600a is around 26% of total refrigerants amount (see *Table 1*).

Taking into account a high demand for refrigerants, their recovery from old equipment can provide more sustainable use of resources and decrease the contribution to global warming. Although, the recovery of some refrigerant blends may be challenging as some of them behave almost like pure fluids with virtually no variation of composition between the vapor and liquid phases and almost constant evaporation/condensation temperature at a given pressure (Asensio-Delgado et al., 2020).

Table 1. *Global use of refrigerants for refrigeration and air conditioning, cumulative data for 2012–2017 (Booten et al., 2020)*

Refrigerant	Weight, thousand tonnes
R22	248–400
R134a	190–240
R125	83
CO_2 (R744)	70–80
Propane (R290)	37–46
R143a	29
R1234yf	15–30
R152a	17
Ammonia (R717)	9–26
R32	10
Isobutane (R600a)	6–11
R142b	6
R143a	1
Total	749–949

In Ukraine, old household fridges are not collected as a waste. They are mainly stored unused or sometimes are illegally disposed of at landfills. This contributes to environmental pollution, global warming, ozone depletion and resource loss.

The purpose of this research is to assess the recovery potential and contribution of refrigerants to global warming through the calculation of their residual volumes in old equipment using Ukrainian household fridges as a case study. In this study, refrigerants use in Ukraine is analysed and refrigerants mass flow for domestic refrigeration is estimated. Besides, greenhouse gas emission (GHG emission) is calculated for waste household fridges.

Methods

The use of refrigerants in Ukraine was analysed through a literature review and open source data analysis. To estimate refrigerant recovery potential, one needs to assess number of refrigeration units. In this study, domestic refrigeration was analysed. For this purpose, the following data were collected:

- statistics on equipment manufactured (available from State Statistical Service of Ukraine);
- data on import/export of household fridges (retrieved from UN Comtrade database (UN)).

For refrigerant mass flow analysis, 42 household fridges (in use) were studied. Type and nominal amount of refrigerant was identified in order to define changes of refrigerants use in time.

The total amount of household fridges placed on the market (POM) can be calculated by the equation (Forti et al., 2018):

$$\mathrm{POM} = \mathrm{P} + \mathrm{I} - \mathrm{E} \quad (1)$$

where P is the domestic production of fridges, pcs; I is the number of fridges imported, pcs; E is the number of fridges exported, pcs.

The amount of waste fridges (W, items) can be estimated according to Eq. 2–4:

$$\mathrm{W} = \sum_{t=t_0}^{n} POM(t) \cdot L^p(t,n) \quad (2)$$

where n is the year for which the calculation is done; t_0 is the initial year that a product was sold; L^p (t, n) is the discard-based life-time profile for the batch of products sold in historical year t.

Similar calculation was previously used for other electronic appliances (Ishchenko and Sydoruk, 2023), and were considered to be relevant if lack of data is a case.

Using the amount of waste fridges, one can assess a refrigerant weight that can be recovered (M):

$$\mathrm{M} = \mathrm{W} \cdot \mathrm{r} \quad (3)$$

where r is the refrigerant residue in a fridge.

For GHG emission calculation, potential emissions of different refrigerants must be estimated. For the conditions of Ukraine, where no collection system is used for waste household fridges, this number is actually equal to the sum of the remaining refrigerants in waste household fridges and refrigerant losses during the equipment operation. Then, GHG emission can be calculated by the following equation:

$$GHG = \sum(L_i + M_i) \cdot a_i \quad (4)$$

where L_i is the refrigerant i losses; M_i is the amount of refrigerant i emission; and a_i is the global warming potential of refrigerant i.

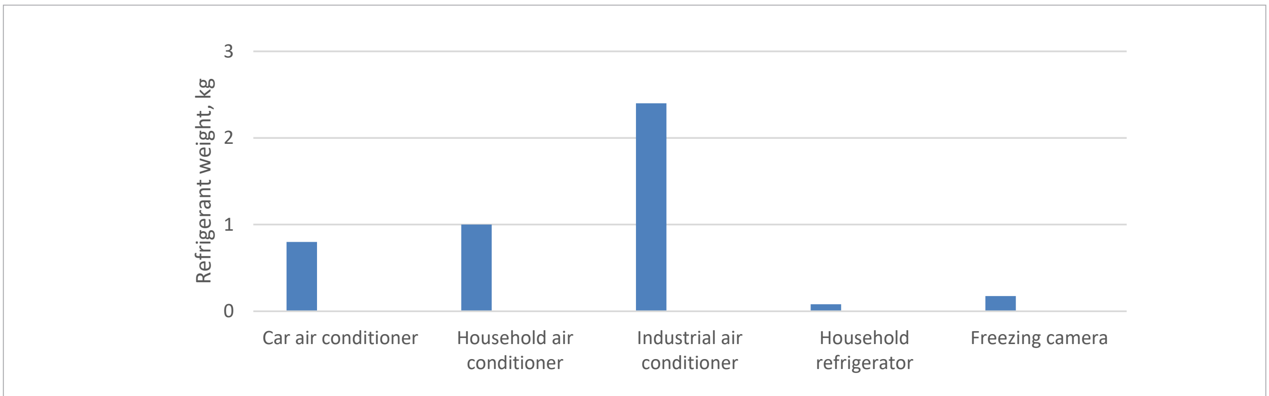
Results and Discussion

Refrigerants use in Ukraine

Refrigerants are most often used in refrigerating equipment, air conditioning systems, and freezing equipment (*Fig. 2*). Basically, the type of refrigerant used depends on the age of equipment available in the country and the import of modern equipment: for the case study of household fridges in Ukraine, R12 is mainly used in old equipment and refrigerants R134a and R600a in new fridges (based on this study). For other countries, it can be slightly different: globally, R410a is the most used refrigerant in domestic air conditioning systems, and R134a is mostly used in cars (Martinho et al., 2022).

The largest volume of refrigerants is used in air conditioners (primarily, of industrial type – up to 2.5 kg per unit), while household fridges contain a fairly small amount of refrigerant. This is also confirmed by other studies (McLinden and Huber, 2020).

Fig. 2. *Average amount of refrigerant in the equipment (based on the data in (Seidel et al., 2015))*



Currently, old-type refrigerants are still in wide use due to its supply for recharging old equipment from refrigerant-producing countries (mainly China and the USA). China remains the main producer of refrigerants, accounting for most of the annual production of chlorofluorocarbons (CFCs). At the same time, the USA is the main producer of hydrofluorocarbon and hydrofluoroolefin refrigerants (R134a and R32). The growth of refrigerants production in China has paralleled the increase in the manufacture of refrigeration and air conditioning equipment. This growth was facilitated by inexpensive raw materials from large-scale mining of fluorspar in China, cheap labour and energy for processing, and the establishment of "centres of excellence" in Chinese chemical production (Seidel et al., 2015).

To adopt EU legislation, the Procedure for submitting reports by operators of controlled substances moved across the customs border of Ukraine and placed on the market entered into force since 2024. According to this document, companies are obliged to record the information on whole life cycle of fluorinated greenhouse gases and ozone-depleting substances (from the moment of border crossing to the final removal or processing). That should provide a more controlled use of refrigerants.

Mass flow of refrigerants

To estimate the loss of refrigerant residues in the end-of-life equipment, one can use the data on original amount of refrigerant in the equipment. As an example, a comprehensive analysis of old household fridges in Ukraine (different years of manufacture and different producers) was conducted (*Table 2*).

Table 2. *Refrigerant use in domestic refrigeration*

Fridge brand	Producer	Year of manufacture	Volume, L	Refrigerant type	Original refrigerant amount, kg
AEG	Italy	2001	396	R600a	0.06
AEG	Italy	2001	361	R600a	0.072
Atlant	Belarus	1987	280	R12	0.14
Atlant	Belarus	1995	90	R600a	0.04
Atlant	Belarus	1995	354	R600a	0.058
Atlant	Belarus	1995	310	R134a	0.115
Atlant	Belarus	1995	360	R134a	0.06
Atlant	Belarus	2002	345	R600a	0.032
Atlant	Belarus	2003	350	R600a	0.045
Atlant	Belarus	2004	345	R600a	0.036
Atlant	Belarus	2004	350	R600a	0.045
Atlant	Belarus	2004	370	R600a	0.056
Beko	Russia	2001	298	R600a	0.046
Beko	Russia	2003	379	R600a	0.054
Bosh	Russia	2001	350	R600a	0.045
Bosh	Germany	2001	318	R600a	0.045
Bosh	Germany	2002	244	R600a	0.092
Candy	Russia	2006	409	R600a	0.081
Daewoo	Russia	2006	330	R134a	0.115
Electrolux	S. Korea	1995	245	R600a	0.043
Gorenje	Slovenia	2000	315	R600a	0.036
Gorenje	Serbia	2001	325	R600a	0.053
Haier	Russia	2017	477	R600a	0.062
Hotpoint-Ariston	Russia	2001	233	R600a	0.063
Hotpoint-Ariston	Russia	2004	325	R134a	0.09
Hotpoint-Ariston	Russia	2004	320	R134a	0.145
Hotpoint-Ariston	Russia	2004	271	R134a	0.098
Indesit	Russia	2001	345	R134a	0.145
Indesit	Russia	2001	280	R134a	0.175
LG	Russia	2011	230	R600a	0.06
LG	S. Korea	2017	230	R600a	0.06
LG	S. Korea	2017	238	R600a	0.061
LG	Russia	2017	213	R134a	0.05
Liebher	Germany	2001	398	R600a	0.064
Liebher	Germany	2002	279	R600a	0.056
Liebher	Germany	2002	499	R600a	0.095
Liebher	Germany	2004	535	R600a	0.04
Minsk	Belarus	1980	200	R134a	0.135
Samsung	S. Korea	2014	535	R600a	0.093
Siemens	Russia	2001	354	R600a	0.053
Siemens	Germany	2001	297	R134a	0.14
Siemens	Germany	2004	275	R600a	0.088

Table 2 shows that the most commonly used refrigerants are R600a and R134a. Some very old household fridges contain R12 refrigerant. Meanwhile, in EU countries, R600a is the most commonly found, while R134a has been phased out since 2014 (Straub, 2018). Generally, refrigerant content ranges from 0.032 to 0.175 kg per item with average value 0.075 kg. Moreover, there is no dependence of refrigerant content on the producer or year of manufacture (but one should take into account a size/volume of the fridge). Although, in the fridges produced after 2010, refrigerant content is well below 0.1 kg/item (see *Fig. 3*). Mainly this is because newer fridges use R600a refrigerant–its average content is lower comparing to R134a: 0.058 kg and 0.115 per item, respectively.

At the same time, the size of the fridge must be also taken into account. As can be seen from *Fig. 4*, a specific amount of refrigerant is generally few times higher in the fridges with R134a (mainly ranges from 0.3 to 0.5 kg/L) comparing to the fridges with R600a (ranges from 0.08 to 0.3 kg/L). This means less refrigerant is used in newer fridges.

It is not possible to estimate the types and age of fridges still in use in households since there is no waste equipment collection. Therefore, the only way to estimate refrigerant amount is to analyse domestic refrigeration market.

In Ukraine, the statistic on household fridges manufacture is available for 2003–2022 (SSSU). Taking into account average lifespan of household fridges (approx. 15 years (Dekoninck and Barbaccia, 2019)), it is relevant to estimate the amount of waste fridges in current years. Along with export / import data from UN Comtrade base (UN), one can calculate the amount of household fridges placed on the market according to the *Equation (1)* (see results in the *Table 3*).

Fig. 3. *Change in refrigerant amount in domestic fridges, Ukraine*

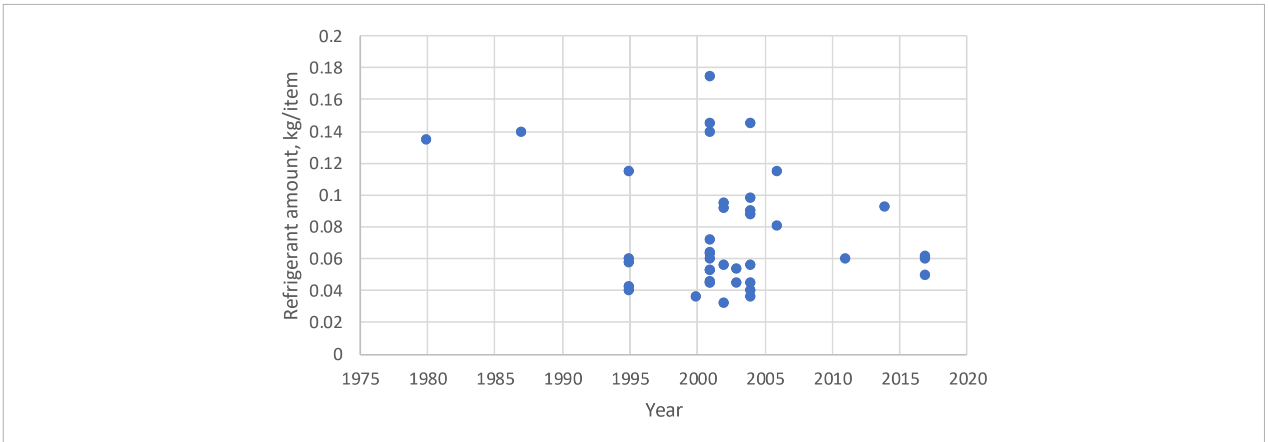


Fig. 4. *Refrigerant amount in domestic fridges (per unit of volume), Ukraine*

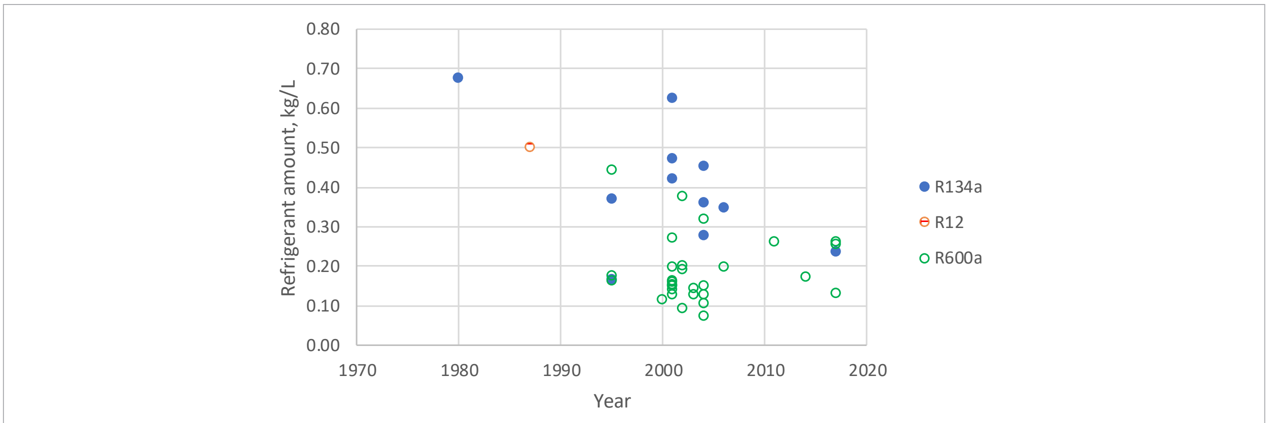


Table 3. *Data on household fridges market, Ukraine*

Year	Fridges manu-facture, pcs	Fridges import, pcs	Fridges export, pcs	Placed on the market, pcs
2003	284,000	368,451	534,942	117,509
2004	269,000	214,513	326,779	156,734
2005	242,000	170,119	242,838	169,281
2006	338,000	95,041	271,090	161,951
2007	310,000	89,919	203,727	196,192
2008	222,000	70,775	164,377	128,398
2009	157,000	27,408	119,450	64,958
2010	164,000	58,272	123,651	98,621
2011	NA	96,379	95,267	1112
2012	NA	110,479	73,549	36,930
2013	NA	95,783	64,847	30,936
2014	NA	61,784	61,239	545
2015	NA	29,639	24,664	4975
2016	NA	46,326	848	45,478
2017	NA	69,289	369	68,920
2018	NA	75,469	286	75,183
2019	NA	86,313	200	86,113
2020	NA	107,830	264	107,566
2021	NA	103,167	584	102,583
2022	NA	58,067	564	57,503

*NA – data not available

It must be noted that household fridges manufacturing since 2011 is not known (there is no statistical data since 2011). This influences the calculation significantly as fridges manufacturing was significant in comparison to import / export.

Based on the *Equation (2)* and using the calculation tool developed by European Commission (WEEE), one can calculate the generation of waste household fridges (see results in the *Table 4*).

For comparison, the total number of waste household fridges in China is estimated at 28.5 million units per year (Li et al., 2019).

There is no data on the number of fridges with certain refrigerant. Therefore, based on the *Table 2*, the number of fridges with R134a refrigerant was assumed to be 27% of the total number, and the number of fridges with R600a refrigerant was 73% (fridges with R12 refrigerant are excluded from the calculations, as they are very rare). Then, according to the modified *Equation (3)*, the amounts of residual R134a and R600a refrigerants are as follows:

Table 4. *Estimated (2020–2023) and forecasted (2024–2030) generation of waste household fridges in Ukraine, 2020–2030*

Year	Waste household fridges, pcs
2020	59,467
2021	61,628
2022	63,471
2023	64,937
2024	65,882
2025	66,261
2026	66,074
2027	65,345
2028	64,110
2029	62,414
2030	60,309

$$M(R134a) = W \cdot 0.27 \cdot r(R134a) \tag{5}$$

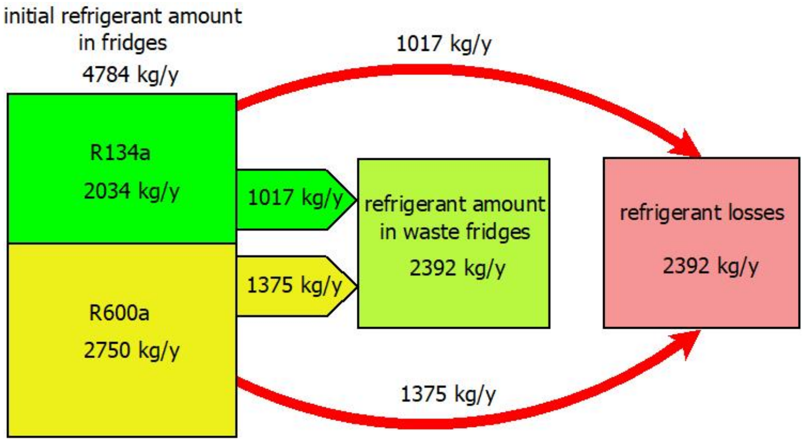
$$M(R600a) = W \cdot 0.73 \cdot r(R600a) \tag{6}$$

According to the South Korea experience of waste fridges collection scheme, averagely 50% of the original refrigerant can be removed from each household fridge (Park et al., 2019). Then, the residual weight of R134a and R600a refrigerants in one fridge can be estimated at 0.058 and 0.029 kg, respectively. Taking into account the number of waste household fridges (*Table 4*), it is possible to estimate the average annual amount of residual R134a refrigerant at about 1 tonne, and R600a refrigerant at 1.4 tonnes (*Fig. 4*).

Fig. 4 demonstrates the material flows of household fridges refrigerants in Ukraine, based on the data in *Tables 3* and *4*, as well as calculations of the residual weight of refrigerants (waste data as of 2023).

From the practice, about 10–20% of recovered refrigerants cannot be recycled (from any equipment). This includes refrigerant recovered after compressor burnout, mixtures of different types of refrigerants, residues from recovery processes (UNEP, 1999; Taib et al., 2019). Thus, refrigerant recovery potential may be estimated at 2 tonnes per year (counting 80% recycling rate). For comparison, 2779 kg of R134a, 2242 kg of

Fig. 4. *Mass flow of household fridges refrigerants*



R12, and 195 kg of R22 were recovered in 2016 in South Korea (Park et al., 2019), mainly from fridges – totally 5020 kg (96.2%).

Calculation of greenhouse gas emission

There is no separate collection of waste electrical and electronic equipment in Ukraine. Partially, few companies provide the collection from some organizations (Hlavatska et al., 2021). Therefore, household fridges are not covered by the waste management system. With a high probability, this results in refrigerants emission (from waste household fridges) to the air, which contributes to the ozone layer depletion and global warming. In the previous section, the amount of residual refrigerants was estimated at 2.4 tonnes/year and is approximately equal to the loss of refrigerants during the fridges operation. In Ukraine, old household fridges are not recycled, therefore both the residual refrigerant and its loss contribute to global warming (a total of 4.8 tonnes/year).

The GHG emission was calculated for the two main refrigerants used in household fridges (*Table 2*) – R600a and R134a. In the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC, 2013), GWPs of R134a and R600a are 1300 and 3, respectively. According to the *Equation (4)*, the total GHG emission of refrigerants used in household fridges is estimated at about 2652 tonnes of CO_2-equivalent/year. This is quite a high GHG amount contributing significantly to Ukraine's total GHG emission. Moreover, the share of R600a refrigerant is only 0.3% (due to its low global warming potential), while R134a refrigerant is the main contributor to global warming despite its lower use. That was also confirmed by Padmavathy et al. (2022). Taking into account new fridges mainly use R600a refrigerant, we can assume that less GHG emission will be generated from domestic refrigeration in coming years.

Conclusions

This study analyses refrigerants use and mass flow for domestic refrigeration in Ukraine. The need for refrigerants in Ukraine remains high. It was revealed that due to the lack of a collection system for old household fridges, residual refrigerants are wasted and make a significant contribution to global warming. At the same time, a significant amount of refrigerants can be recovered. R600a and R134a refrigerants are found to be the most widely used with average original weight in household fridges of 0.058 and 0.115 kg per item, respectively. There is a lack of data on waste fridges collection in Ukraine. Therefore, average lifespan of household fridges, and export / import data can be used to calculate the amount of household fridges and, thus, amount of waste refrigerants. Taking into account refrigerant leakages, the recovery potential of R600a and R134a refrigerants from household fridges was estimated at about 2 tonnes/year. Although the need for refrigerants recovery in Ukraine is quite high, this technology is currently not used due to the lack of a market for secondary refrigerants and old equipment collection. Waste electrical and electronic equipment, including household fridges, is not collected separately in Ukraine. Manufacturers and retailers have no motivation and funds to recycle old equipment. In near future, establishing an extended producer responsibility for electrical and electronic equipment is expected due to EU regulations implementation. This should enhance a significant increase in electronic waste processing and, thus, recovery of refrigerants from such equipment is expected. This will also help to reduce the contribution of domestic refrigeration to global warming, which is currently estimated at about 2652 tonnes of CO_2-equivalent/year with R134a refrigerant as the main contributor. Summarizing the findings, it must be noted that local/regional/national monitoring and collection system for waste fridges are needed in order to estimate more comprehensively the resources that can be recovered.

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