# New Low-GWP Refrigerants Analysis with Gas Chromatography

## 1 Background & project overview

Refrigeration is named one of the "twenty most significant engineering achievements of the 20th Century" (Constable & Somerville, 2003), (McLinden & Huber, 2020), and is an inevitable element in the society today. Refrigerants (i.e., the refrigeration medium used in both heat pumps and refrigeration systems) have evolved over the years, now emerging into the 4th generation (McLinden & Huber, 2020). The first generation of refrigerants were 'whatever that worked', e.g. ammonia, propane, $CO_2$, and even $SO_2$ as (McLinden & Huber, 2020) present, used from the beginning of artificial refrigeration until 1930s. During 1930-1995 the now 'notorious' and phased-out chlorofluorocarbons (CFCs) were the most used, e.g. R-11, R-12 and R-22 (c.f. ASHRAE Refrigerants designations (ASHRAE, 2021), deemed safe for being non-flammable, non-toxic and durable (Palm, 2021), (McLinden & Huber, 2020). The CFCs, commonly commercially termed as Freons, were used as pure components (not blends) (Palm, 2021), and are the 2nd generation refrigerants (McLinden & Huber, 2020). The eventual discovery of the influence of CFCs to deplete the Ozone layer in the stratosphere led to their phasing out (Palm, 2021). This led to the 3rd generation; synthesizing molecules without the chlorine atom, which is the culprit for Ozone depletion, thus resolving to hydrofluorocarbons (HFCs), e.g. R134a and R32 (Palm, 2021).

These HFCs unfortunately have significant global warming potential (GWP) (Palm, 2021), (McLinden & Huber, 2020) thus are being phased out within this decade. This gave rise to resolving to less stable refrigerants in the 4th generation, such as in hydrofluoroolefins (HFOs) (McLinden & Huber, 2020), e.g. R1234yf and R1234ze(E) (Palm, 2021). With difficulties in finding suitable refrigerants that are e.g. non-flammable and have a low GWP, for certain applications, the industry introduced the use of some of these refrigerants in blends (mixtures), in place of the previous alternatives (Palm, 2021). Some such refrigerants defined as blends are e.g. R448A and R464A (Palm, 2021) (ASHRAE, 2021). Some of these blends however are non-azeotropic, meaning that they risk of undergoing compositional changes when they are recharged or leaked to/from the systems (due to the compositional differences of the blends in liquid and vapor phases) (Palm, 2021).

In this context, in this master's thesis project, the aim is to investigate if such refrigerant blends circulating in heat pump and refrigeration systems in real-life installations have the compositions that are expected (as per their original conditions). A state-of-the-art Gas Chromatograph (GC): Trace 1310 (from Thermo Fisher) has just been procured (see Figure 1) by the division of Applied Thermodynamics and Refrigeration (ETT), and is intended to be used in these investigations. The GC consists of a flame-ionization detector (FID) and a thermal sensitivity detector (TCD), with, a porous polymer column. A number of real-life heat pump and refrigeration installations (from e.g. supermarkets, industries and district heating/cooling installations, etc.) will be chosen as 'sampling sites'. Upon establishing contacts within these chosen entities, refrigerant samples will be collected, transported to the ETT lab and analyzed in the GC, upon successful calibration and analysis procedure establishment. The obtained results will be then compared against their expected original compositions and thereby key engineering and scientific conclusions will be drawn. The student will work, in this project, closely together with the supervisor, reference group and the examiner, as relevant and needed. In the thesis report, the student needs to critically and comparatively discuss these results on the contexts of refrigeration technology as well as sustainability.

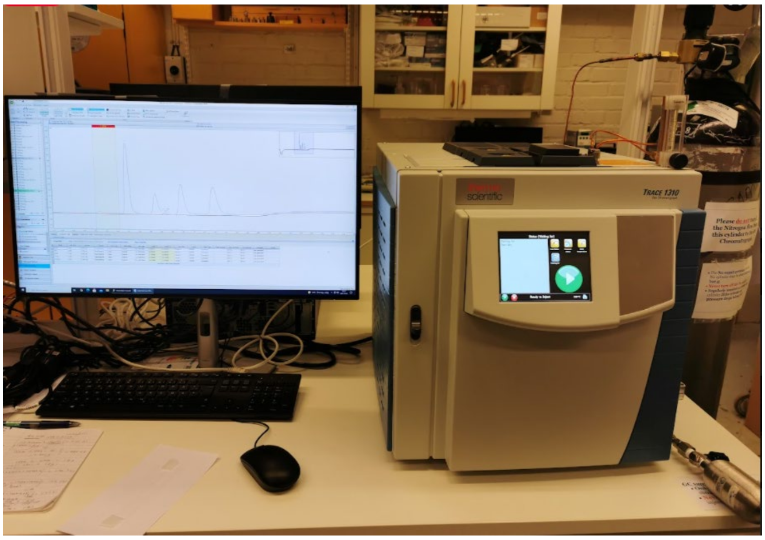

*Figure 1. The state-of-the-art GC (Trace 1310) to be used in this project (at Applied Thermodynamics and Refrigeration division)*

## 2 Thesis learning objectives

After the thesis project is performed, the student(s) should be able to/should:

- Perform a literature survey on a given study scope (on refrigerants including both natural and synthetic types, current state-of-the-art and trends in finding new low-GWP refrigerants) through an effective and efficient screening of relevant literature to understand the underlying theory and concepts within a short period of time
- Plan and execute the safe and accurate collection of refrigerant blend samples from several chosen real-life commercial and/or industrial heat pump and refrigeration systems and their safe transport as pressurized gases/fluids
- Knowledgeable on hands-on experience in refrigerant gas mixture analysis methodology development and analysis in a Gas Chromatograph equipped with a flame-ionization detector (FID) and a thermal sensitivity detector (TCD), on a porous polymer column
- Knowledgeable and self-sustained in post-processing and evaluating the obtained experimental results from the GC measurements
- Critically and comparatively discuss the obtained experimental results, any deviations which may be identified in the measured concentrations versus original/expected concentrations, with possible reasons and mitigation, and the implications of these results on the current state of the art on refrigeration technology
- Generalize the obtained results and their implications into the contexts of sustainability
- Seek advice effectively and perform the research tasks independently when necessary, and take initiatives as necessary for the progress of the project
- Draw key engineering and scientific conclusions based on the critical analysis of the obtained results, and therein, propose relevant future work to improve these measurements and also suggestions to address any concentration deviations identified through the analyses.

## 3 Method of attack

The proposed methodology for this thesis work includes the following. It should start with an effective screening of relevant literature and documentation of the relevant findings (on refrigerants including both natural and synthetic types, current state-of-the-art and trends in finding new low-GWP refrigerants), concisely yet effectively, to understand and explain the underlying theory and concepts. Thereafter, full engagement in all the necessary hands-on steps for the refrigerant blends samples collection from the field (i.e., from several real-life commercial and/or industrial establishments using heat pump and

refrigeration systems, which will also be decided within the project) is necessary. Upon successful collection and transport of the samples to KTH, the next step is performing experimental measurements of these blends in the GC (also together with other involved researchers, as required) on a methodology that is developed. Each measurement of an unknown gas blend should be preceded by a calibration procedure to include the components and their approximate composition ranges expected in the blend. Correct and consistent data post-processing and evaluation of these results should follow next. These evaluated results then should be critically discussed comparing against their original (i.e., at the time of commissioning of the heat pump/refrigeration system) or expected compositions. The thesis project and its outcomes should also be discussed along sustainability aspects. Overall engineering and scientific conclusions should be drawn, in the end. The thesis report writing must be a continuous process parallel to the project work, from the very beginning to the end. Maintaining and updating a realistic thesis project time plan is also a must, throughout the project.
The thesis report(s) should be written in English, supplemented by a Swedish summary (sammanfattning), while the student should have sufficiently good writing skills to write a clear and a comprehensible master's thesis report.

**The thesis project can be done also by 2 students collaborating with the experimental tasks, after discussing the different scopes for their individual contributions, submitted in two separate thesis reports**.

## 4 Pre-requisites

- Refrigeration/ Chemical/Material/Thermal/Mechanical Engineering or similar background.
- Knowledge and preferably experience in gas chromatography and/or the involvement in real-life or experimental refrigeration/heat pump systems operation.
- Fundamental knowledge on chemistry related to gases and their mixtures, refrigeration technology
- Very good English proficiency, both oral *and written*

## 5 Preliminary proposed time schedule, with milestones and report deadlines

**Expected** to **start** the work by **March 2022 (but is flexible)**

The thesis project is planned for a time span of maximum 6 months. This is roughly allocated as (up for discussion):

1. Find and screen through relevant literature to understand and document the underlying theory and concepts: 2-3 weeks (1$^{st}$ month)
2. Selection of, finding contact details of, and establishing contacts with, several suitable real-life commercial and/or industrial establishment with heat pump and refrigeration systems: 2-5 weeks (1$^{st}$-2$^{nd}$ month)
3. Plan and execute the safe and accurate collection of refrigerant blend samples from these chosen heat pump and refrigeration systems and their safe transport as pressurized gases/fluids: ~13 weeks (1$^{st}$- 4$^{th}$ month)
4. Find the expected or original compositions of these gas blends that are collected (via the suppliers, chosen installation operators, (ASHRAE, 2021), literature, or like): ~16 weeks (1$^{st}$ – 4$^{th}$ month)
5. The analysis methodology development and analysis of suitable calibration mixtures and dilutions as well as these collected gas mixtures in the GC: ~16 weeks (1$^{st}$-5$^{th}$ month)
6. Upon obtaining successful measurements on each unknown blend, performing post processing of the data: ~15 weeks (2$^{nd}$-5$^{th}$ month)
7. Mid-term report submission (beginning of the 3$^{rd}$ month)

8. Based on the gas mixture measurements in the GC and their data analysis, draw critical discussion points: ~11 weeks (3rd month-6th month)
9. Bring forward overall critical discussions and conclusions comparing the project findings with findings from literature also including similar/comparative analyses and overall in-terms of suitability aspects: ~10 weeks (4th-6th month)
10. Report writing ~18 weeks (mid of 1st month to mid of 5th month)
11. Final thesis presentation preparation: 1-2 weeks (5th -6th month)
12. Final thesis (draft) report submission: end of 5th month, final thesis defense: ~end of 6th month, absolute final report submission: ~end of 6th month

**A rough and tentative time plan is as below (some potential holidays are excluded as e.g. in grey):**

| ↓Step/ →month | January | February | March | April | May | June |
|---|---|---|---|---|---|---|
| **1** | | | | | | |
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| **12** | | | | | | |

# 6 Supervisor, Reference Group and Examiner at KTH, Department of Energy Technology:

## Supervisor (and Contact):

Dr. Saman Nimali Gunasekara (saman.gunasekara@energy.kth.se)
**Office:** +46 (0)8790 7430, **Mobile:** +46 736 523 339

## Reference group:

Mr. Peter Hill; Ms. Monika Ignatowicz, and Prof. Björn Palm

## Examiner:

Prof. Björn Palm

# 7 Application

If you are interested and feel that you fulfill the pre-requisites: send in your applications **to Saman** with **CV, cover letter and academic transcripts for both bachelor's degree and master's degree** (so far). (Your cover letter will be assessed also as a measure of your English proficiency).

# 8 References

ASHRAE. (2021, May 25). *ASHRAE REFRIGERANT DESIGNATIONS*. (ASHRAE, 80 Technology Parkway NW, Peachtree Corners, Georgia 30092 US) Retrieved February 02, 2022, from https://www.ashrae.org/technical-resources/standards-and-guidelines/ashrae-refrigerant-designations

Constable, G., & Somerville, B. (2003). *A Century of Innovation: Twenty Engineering Achievements that Transformed our Lives.* Washington, DC: John Henry Press: , 2003.

McLinden, M. O., & Huber, M. L. (2020). (R)Evolution of Refrigerants. *Journal of Chemical Engineering Data, 65*, 4176–4193. doi:https://dx.doi.org/10.1021/acs.jced.0c00338

Palm, B. (2021). Personal Communication- The Evolution of Refrigerants. Stockholm: KTH Royal Institute of Technology.