Which Hydrocarbons Can Be Used as Refrigerants?

We regularly hear about new products using **hydrocarbons** as refrigerants. These do not come only from small, enthusiast-driven companies—several **major manufacturers** are now launching such products as well [1–5]. Most of these systems are intended for **outdoor installation**, but at least one manufacturer, **Ecoforest**, offers **indoor ground-source heat pumps** containing **150 g** of refrigerant [6]. All of these manufacturers use **propane** as the refrigerant in their products; at the same time, we know that **household refrigerators and freezers** commonly use **isobutane**.

A number of other hydrocarbons could also be used. In this column, we compare different hydrocarbons that may be suitable as refrigerants in heat pumps and refrigeration systems.

Criteria for Selecting a Refrigerant

Historically, choosing a refrigerant was simpler, as far fewer options existed. The underlying criteria, however, are largely the same today:

• Suitable pressure level

We want the system to operate within reasonable pressure limits. Traditionally, this meant operating **above 1 bar** (to prevent air infiltration) and **below 25 bar**. Today, we avoid sub-atmospheric pressures mainly because **low suction pressure implies large volumetric flows** and therefore **large compressor displacement**.

We have also become accustomed to working with high-pressure refrigerants such as **R410A, R32, and CO_2**, which operate at much higher pressures than earlier systems.
The **normal boiling point (NBP)** at atmospheric pressure provides a rough indication of the expected pressure level:
Lower NBP → higher pressures at a given temperature.

• Low discharge temperature

A low discharge gas temperature is desirable to span a large temperature lift without degrading compressor oil. In general, **more complex molecules** (with more atoms) yield **lower discharge temperatures**, though they typically suffer from higher throttling losses and may benefit more from subcooling.

• High COP

For comparing refrigerants, a simple cycle without subcooling or superheating can be used—but this does **not provide the full picture**.
Some refrigerants experience significant COP increases with **subcooling** or with an **internal heat exchanger (IHX)**, while others do not. Performance differences also depend strongly on the intended **temperature levels**.

In general:
Low-pressure refrigerants → somewhat **higher COP**
High-pressure refrigerants → **higher volumetric capacity**, enabling **smaller compressors and narrower pipes**.

• Critical temperature (T_{kr})

The critical temperature strongly influences COP. If the condensing temperature approaches $\mathbf{T_{kr}}$, COP drops.
Thus, for applications requiring high output temperatures, a refrigerant with **high critical temperature** is preferred.

• Thermophysical properties

Important properties include:

- Low viscosity → low pressure drop
- High thermal conductivity → small temperature differences in heat exchangers
- Low pressure ratio at given temperatures → high compressor efficiency

• Material compatibility

The refrigerant must be compatible with **metals and polymers** (gaskets, insulation, etc.).

• Safety

We seek **low flammability** and **no toxicity**.

• Availability of suitable oil

The refrigerant must have a compatible compressor oil—often a challenge for experimental or new refrigerants.

All of these factors must be considered when comparing refrigerants.

Which Hydrocarbons Are Potential Candidates?

The standard reference for refrigerant properties, **NIST REFPROP**, lists **24 hydrocarbons**. Many of these are unsuitable due to boiling points that are either too low or too high for typical heat-pump applications.

Restricting ourselves to hydrocarbons with **NBP between that of R32 (high pressure) and R245fa (low pressure)** yields **8 candidates**. Hydrocarbons with **1–2 carbon atoms** have too low NBP; hydrocarbons with **5+ carbon atoms** have too high NBP.

Table 1 presents key data for these eight hydrocarbons, together with two HFCs for comparison, ordered from high-pressure to low-pressure refrigerants.

		Normal kokpkt	Tryck vid 45C	Tryck vid -5C	Tryck förhållande	Hetgastemp	Ånghalt	Molmassa	Kritisk temp	Kritiskt tryck	Termisk ledn, vätska, -5C	Termisk ledn, gas, -5C	Ångbildnings värme	Viskositet, vätska, -5C	Viskositet, vätska, -5C	Utan uk el öh	Med 5K ukyl o intern vvx	Lägre antänd ningsgräns
Medium	Beteck	NBP	p1	p2	p1/p2	T1k_is	x	M	T_kr	P_kr	k_liq	k_vap	r	my_lic	my_va	COP1	COP1	LFL%
		°C	MPa	MPa		°C			°C	MPa	mW/	mW/n	kJ/kg	µPa s	µPa s			
R32	R32	-51,7	2,79	0,691	4,05	84,0		52,0	78	5,8	149	11,3	323	159	11,28	4,9	5,1	14%
propen/propylen	R1270	-47,6	1,84	0,502	3,67	56,4		42,1	91	4,6	128	14,5	385	127	7,66	5,0	5,2	1,8%
propan	R290	-42,1	1,53	0,406	3,78	50,8		44,1	97	4,3	109	15,2	382	132	7,30	5,0	5,2	1,7%
cyklopropan 0/50C	RC270	-31,5	1,35	0,344	3,91	68,3		42,1	125	5,6	129	14,3	442	157	8,44	5,4	5,6	2,4%
dimetyleter	RE170	-24,8	1,01	0,223	4,53	58,7		46,1	127	5,3	137	15,2	441	168	8,53	5,3	5,5	2,7%
isobutan	R600a	-11,7	0,60	0,131	4,61	45	97,0%	58,1	135	3,6	101	13,8	359	210	6,74	5,1	5,4	1,5%
isobuten/isobutylen		-7,0	0,54	0,110	4,90	45	99,9%	56,1	145	4,0	113	14,5	390	209	7,21	5,3	5,5	1,6%
1-buten/butylen	R1390	-6,3	0,52	0,107	4,91	46,7		56,1	146	4,0	113	14,0	391	210	7,29	5,3	5,5	1,2%
butan	R600	-0,5	0,43	0,085	5,10	45	97,6%	58,1	152	3,8	118	13,7	390	213	6,65	5,3	5,5	1,4%
R245fa	R245fa	15,1	0,29	0,042	7,03	45	98,1%	134,1	154	3,7	97	11,0	207	619	9,40	5,3	5,5	N/A
									Värden för cyklopropan gäller vid T1=50C och T2=0C									

Performance Comparison

To proceed, we must define an application. Assume:

- **Evaporation temperature:** −5 °C
- **Condensing temperature:** +45 °C
- **No subcooling or superheating**

Discharge temperature

Assuming **isentropic compression** (actual temperatures would be higher), several hydrocarbons with high NBP (i.e., low pressure) exhibit **little or no superheat** after compression.
For three hydrocarbons, part of the vapor ideally enters the **two-phase region** during compression. For example, with isobutane, the **vapor quality** after isentropic compression is **97%**.

In reality, with non-ideal compression, liquid formation is unlikely, but at large pressure ratios it is wise to verify using realistic isentropic efficiencies.

As expected, **more complex molecules** show **lower discharge temperatures**. None of the eight hydrocarbons yields particularly high discharge temperatures. The calculated value for **cyclopropane** is somewhat higher, but **R32** has **much higher discharge temperatures** than all hydrocarbons.

COP without subcooling

We compute COP for a simple cycle with isentropic compression. For cyclopropane, REFPROP does not provide data below 0 °C, so calculations used **0/50 °C** instead of −5/45 °C.

The table and associated diagram show a trend:
COP increases with increasing NBP (i.e., decreasing pressure level).

Propanes and propene yield identical COP values; all other hydrocarbons deliver **higher COP**. Cyclopropane gives the **highest COP**, though slightly overestimated due to the alternative temperature pair.

COP with 5 K internal subcooling

Assuming an internal heat exchanger providing **5 K subcooling** to the evaporator:

- COP increases for **all** refrigerants
- The ranking remains nearly unchanged
- Hydrocarbons benefit **more** than R32
- Propane and propene still perform lower than the other hydrocarbons

Figure 1 shows COP values for hydrocarbons between R32 and R245fa.

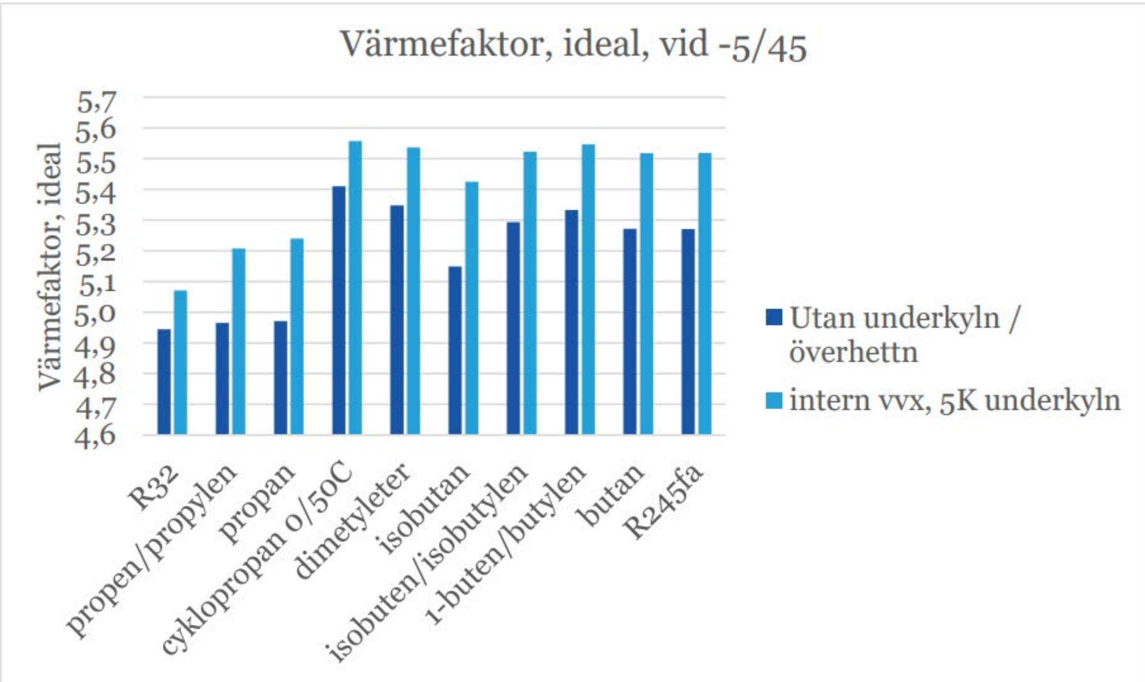

Figure 1. COP values for hydrocarbons with pressure levels between R32 and R245fa (included for comparison), under −5/45 °C conditions, with and without internal heat exchanger (5 K subcooling).

Pressure Ratio and Critical Temperature

As the table shows, increasing NBP (decreasing pressure level) yields increasingly **higher pressure ratios** for hydrocarbons (except cyclopropane). A higher pressure ratio often implies **lower isentropic compressor efficiency**, giving high-pressure refrigerants an advantage.

A **high critical temperature** is advantageous because COP decreases as the condensing temperature approaches T_{kr}.
Low-pressure refrigerants generally have **higher T_{kr}**, making them suitable for **high-temperature heat pumps**.

Other Thermophysical Properties

From the table:

- All hydrocarbons have **higher latent heat of vaporization** than the two HFCs—typical for hydrocarbons.
- Cyclopropane and dimethyl ether show **high latent heat** and **excellent liquid thermal conductivity**, along with propene.
- Liquid viscosity increases with NBP; gas viscosity shows no clear trend. Hydrocarbons have **lower gas viscosity** than HFCs.

Flammability

Lower flammability limit (LFL) values show **no significant difference** among hydrocarbons. All are **highly flammable** and must be handled accordingly, both in installation and during servicing.

Conclusion

There are **several hydrocarbons** beyond propane and isobutane that could be used as refrigerants.
Cyclopropane and **dimethyl ether** stand out with several **favorable properties**, while still operating at pressure levels between propane and isobutane.

As an anecdote: the refrigeration laboratory at KTH has operated a refrigerator charged with **cyclopropane** for **over 20 years**.

References

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