Hydrocarbons as Refrigerants—A Review

J.H. KOH¹, Z. ZAKARIA¹ AND D. VEERASAMY^{2*}

Refrigerants used in air conditioning and refrigeration (AC&R) industries have come full circle since the beginning of the industrial revolution. With concern on issues relating to the environment such as the global warming and climate change issues, we should find a better alternative than to continue using these refrigerants that cause global warming and ozone depletion. AC&R industry players have blended in by introducing some new equipment and components that are specifically designed for hydrocarbon (HC) use. Most new refrigerators sold in Malaysia are already equipped with isobutane [a hydrocarbon designated as R-600a by the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) standards] as refrigerants. Malaysia has ratified the Montreal Protocol and targetted a 10% reduction in hydrochlorofluorocarbon (HCFC) consumption, beginning 2016 with the banning of 2.5 horsepower (hp) and below in air-conditioning (AC) equipment to be used. Instead, hydrofluorocarbon (HFC) R-410a was introduced as a replacement for HCFC- 22, whereas in other countries this HFC has been phased down. This article was initiated because of the difficulty in finding a replacement for HCFC. Also, the possibilities of using HC as an alternative to replace HCFC instead of using HFC as a transitional refrigerant in place of HCFC is reviewed in this article. The performance of HC is very similar to HCFC and flammability issues could be easily overcome with the use of an effective design. Their use could be facilitated with the adaptation of specific standards and properly enacted legislation.

Key words: Refrigerants; hydrocarbon; hydrochlorofluorocarbons; hydrofluorocarbon; flammability hydrofluorocarbon

Malaysia has committed to the reduction in the consumption of hydrochlorofluorocarbons (HCFC) and other ozone depleting substances following the ratification of the Montreal Protocol on 29 of August 1989. The Department of Environment (DOE) Malaysia, has devised the HCFC Phase-out Management Plan by gradually reducing the dependency, starting with the reduction of 10%, 35%, 67.5 % and total phase out for the year, 2015, 2020, 2030 and 2040, respectively with only minimal quantities usage for servicing purposes (DOE 2010).

With this implementation, the local air conditioning and refrigeration (AC&R) industry is subjected to a plan and imposed restriction by DOE to ban the manufacture, importation and installation of split type air conditioner units of 2.5 horse power (hp) (cooling capacities of 24 000 British thermal units per hour (BTU/h) and below) as of 31 December 2015 (DOE 2015).

The AC&R players have also resorted to converting the manufacturing, importation, and installation of AC&R equipment from HCFC 22

¹ Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Skudai, Johor, Malaysia

² Suraaj Mahir Consultancy, 19, Jalan KE 4/9, Kota Emerald, 48000 Rawang, Selangor, Malaysia

* Corresponding author (e-mail: veerasamydevaraj199@gmail.com)

to hydrofluorocarbon (HFC) 410a, citing the “0” ozone depletion potential (ODP), as its distinct advantage. The HFC 410a equipment was often being labelled as eco-friendly despite having a Global Warming Potential (GWP) of 2090 as compared to HCFC 22, which is at 1810.

At least one major AC&R equipment manufacturer has introduced HFC 32 or R 32 (difluoromethane), a mildly flammable refrigerant as the answer to the replacement refrigerant to HCFC 22. The advantages HFC 32 has over the HFC 410a is the low GWP (675) and lower volume needed to produce the same refrigeration effect as HFC 410a. However, the cost of the new equipment, higher operating pressures, and the mild flammability will be of significant concern to the end users. Beside these R 32 has an atmospheric lifespan of 5.2 years and when leaked to the environment has long effect of 675 times more potent than CO₂ has, as a global warming gas.

Most domestic refrigerators sold in Malaysia these days consist of hydrocarbon (HC) refrigerants with isobutane (HC 600a) as a clear choice due to similar thermodynamic properties it had with the HFC 134a refrigerant which it replaces. In the refrigerators, the insulation materials also consist of cyclopentane as its blowing agent. *Figure 1* shows the Japanese branded refrigerator currently being sold in a local Malaysian departmental store using isobutane (R 600a) as a refrigerant and cyclopentane (C₅H₁₀) as its insulation blowing agent. It has the highest energy efficiency ratings of “5 Stars” awarded by the Energy Commission of Malaysia. Fire hazard warning labels are found throughout the back of the refrigerator to inform owners and handlers of the potential risk of fire when using or to repairing the fridge.

However, in the air conditioning sectors, the use of HC refrigerants is at the minimal as there is no equipment manufactured or imported suited for use. The Fire and Rescue Department of Malaysia only allows equipment that is manufactured specifically to use HC and prohibits any form of HC “drop in” to replace HCFC 22. Any modification to existing equipment that uses other than HC shall only be allowed to operate if professional engineers certified the safety aspect.

In the European Union (EU), HFC is currently being phased down due to its high GWP values. The fluorinated gas regulation (Regulation EU No 517/2014 or commonly addressed as the F-gas regulation) was introduced in 2014 to reduce the EU’s consumption of fluorinated gases gradually, members of the EU have started using natural refrigerants in replacement of HFC. Ammonia, carbon dioxide, water, air and hydrocarbons which are known as “the natural five” have been a much sought-after replacement for the HCFC and HFC they replace. In Malaysia, ammonia (NH₃) refrigeration have long existed in refrigeration systems in the ice making industries. CO₂ would not be efficient in high ambient temperature tropical climates (Lorentzen 1995). Water-lithium bromide (Li Br₂) absorption refrigeration systems are only viable in areas or building which have an abundance of waste heat as it is also not economical and inefficient to supply heat to generators. There are cases of modification and drop in use of HC refrigerants in small scales throughout Malaysia but its impact is minimal to the majority of AC&R players. HC refrigerants are currently being imported from Australia, Korea, and the USA and these products are sold under different trade names. These HC refrigerants are marketed as pure

Figure 1. (a) Two door Japanese brand refrigerator available locally;
(b) fire hazard label with refrigerant identity displayed on the compressor unit;
(c) '5 star' rating label awarded by Energy Commission and
(d) fire hazard labelling on the back of the refrigerator.

refrigerant grade propane and butane which as claimed by importers are made to suite ACR equipment. There are no local manufacturers of ACR equipment using commercially available HC such as liquefied petroleum gas (LPG) as refrigerants, even though the LPG is produced locally.

Elsewhere in China, Yang and Wu (2013) reported that HC (R 290) split ACs produced by a major manufacturer branded as 'GREE' are already being certified by VDA

(Verband Deutscher Elektrotechniker). As of September 2010, and ten months later the ACs manufactured by GREE has obtained the TUV (Technischer Überwachungs Verein) safety certifications. These ACs were slated for export to the European countries especially to Germany. This shows the acceptance of use the of HC based refrigerants in developed countries.

In India, Rajadhyaksha *et al.* (2015) reported that since 2012, Indian ACR equipment manufacturer Godrej and Boyce has launched

its first R 290 based split air conditioners and have since sold and installed around 100 000 units of dedicated R 290 split ACs within the Indian market. The percentage of complaints of insufficient cooling were same as the split ACs using R22 units sold. Complaints of HC leaking from outdoor units was about 0.3%, and no leakage was ever found in the indoor. It was reported that the leaks were mainly from the service valves, condenser and compressor piping.

Developing countries had until now transitioned from HCFCs to HFCs because of the ratification of the Montreal protocol. This transition of using a refrigerant that contains higher GWP values as compared to the one it replaces has been phase down by countries in the EU caucus when the F-gas regulations were enforced thus gradually reduces the use of HFCs. In the case of Malaysia, it allows new AC&R equipment to use HFC 410a as a replacement for HCFC 22 since there are no alternatives.

Developed nations and most recently the 'Significant New Alternative Policy' (SNAP) of the U.S. Environmental Protection Agency (EPA) on March of 2015 has approved low GWPs refrigerants ranging from 3 to 675 to replace existing refrigerants with GWPs ranges of 1400 to 4000. HC refrigerants are included in these categories of refrigerants (US EPA 2015). The question now is, when will the developing nations, like Malaysia follow suite?

Malaysia has the potential to use HC as refrigerants as HCs are currently being produced locally, and the cost will be a non-issue if safety concerns are rectified by adopting safety standards and regulations practiced in several developed countries.

It is the objective of this paper to report on the availability of HCs as replacements for the transitional HFC currently being promoted by the authorities for use in small split type household air conditioners. This paper focuses on the use of HCs as an alternative replacement refrigerants to be used in residential air conditioners and refrigerators.

A Brief History of Refrigerants

Stored ice was probably the very first attempt to provide refrigeration to prevent food from turning rancid. Perkins was the first person credited to create a vapour compression cycle using ethyl ether (Calm & Didion 1998). Other earlier refrigerants in vapour compression cycles include, methyl ether, carbon dioxide, carbon tetrachloride, ammonia, isobutene, propane, dielene, and petrol (gasoline). Without the invention of a hermetic system at that period, industrial accidents were prone due to leaks from refrigeration circuits. (Calm & Didion 1998).

Due to the combustibility and toxicity of early refrigerants, Thomas Midley Junior and Albert Leon successfully synthesized "dichlorodifluoromethane" the world's first chlorofluorocarbon (CFC) in the 1930s and marketed it through Fridgaire, a division of General Motors. It was known as Freon-12 (Designated as refrigerant R 12 by ASHRAE).

Then 40 years later when Molina and Rowland (1974) reported in the *Journal of Nature* that depletion of the stratospheric ozone due to the use of CFC. (Calm & Didion 1998). Ozone Deletion Factor (ODP) of Freon-12 (CFC 12) is 1, and all other refrigerants use CFC 12 as a reference point to determine its potential towards ozone depletion.

The quest for alternatives to CFC and hydrofluorochlorocarbon (HCFC) thus begins with the impending phaseout of these refrigerants through the ratification of the Montreal Protocol in 1989 by all countries that are members of the United Nations.

Chemical companies tried providing solutions in the form of hydrofluorocarbons (HFC) but were later curtailed due to the high GWP values and will also be banned by the ratification of the Kyoto Protocol (1997) and in the European Union, where the commonly known F-Gas regulation prohibits the use of refrigerant with high GWPs. Given the restrictions imposed by the F-Gas regulations, chemical companies tried to blend HFC/HFO mixture to provide alternatives to R 134a, R 404a and R 410a. (Babiloni et al. 2016). Blends like ‘XP-10’ which consists of 44% mass of R 134a and 56 % of R 1234yf is to replace R 134a mainly used in refrigerators and mobile air conditioners. Honeywell proposes blend ‘L 41’ which is 3.5 % mass of R 125, 60% R 32 and 28.5% R 1234ze as a replacement for R 410a currently being used by most split air conditioners (Babiloni et al. 2016).

The quest for low GWP and 0 ODP refrigerants has pushed chemical companies to synthesised a new type of hydrofluoroolefins (HFO). HFO 1234 yf (GWP =4) is to replace the high GWP HFC 134a (GWP =1430) in all vehicles manufactured in European Union (EU) as of 1st January 2017 (EU Mobile Air Conditioning Directive 2006/40/EC). Others tried to blend existing HFC and HFO to overcome the directive of using low GWP and 0 ODP refrigerants in equipment. “Daikin” a major AC&R equipment manufacturer of Japan has encouraged the use of HFC 32

(difluoromethane) which has a GWP of 675 as the main refrigerant to replace HCFC 22. HFC 32 is 50% of HFC 410a which consist of 50% HFC 125 and 50% HFC 32. HFC 32 is a mildly flammable refrigerant as categorised by ASHRAE *Standard 34* and *ISO 817* as ‘A2L’.

On another note, most Scandinavian countries had begun using natural refrigerants to replace synthesised refrigerants in the early 1990s. Ammonia (R 717) has all the while being used in ice making plants and water (R 718) is widely used as a refrigerant in absorption chillers. The use of CO₂ (ASHRAE designated refrigerant no. R 744) in transcritical cycles was conceptualised by Lorentzen (1994), and now more refrigeration units in supermarkets in Europe had adopted this system. Lorentzen (1995) also predicted the re-introduction of natural refrigerants correctly in the foreseeable future to replace all synthesised substances. Hydrocarbon refrigerants which include HC 290 (propane), HC 600a (isobutane), HC 1270 (propylene) and HC 170 (ethane) have now made an impact as an efficient alternative to replace HCFCs and HFCs. HCs are categorised as “A3” by ASHRAE *Standard 34* and *ISO Standard 817* because of inherent flammability.

The use of refrigerants in the ACR industries had witnessed an about turn when in the early 1930s natural refrigerants were widely used before the introduction of CFC, HCFC, HFC, HFO were re-introduced due to climate change. *Figure 2* illustrates the cycle of refrigerant usage from naturals to synthetics and possibly back to natural refrigerants again shortly. The limit of its use back in the 1930s was due to unavailable equipment, knowledge, standards and legislation that made these substances dangerous to operators,

Figure 2. Cycle of refrigerant usage.

building, owners and occupiers. Today we have ‘ATEX’ certified hermetically sealed compressors {ATEX certified is the French term for equipment for use in the explosive environment. (*Appareils destinés à être utilisés en ATmosphères EXplosibles*)}, combustible gas leak detectors, standards and guides to provide a safer environment to use these flammable gasses. The use of refrigerants has witnessed a complete cycle of events that began with using naturally available substances to using synthesised ones and back to natural refrigerants. Calm (2008), provided a historical review of the use of refrigerants from 1st generation utilized in the 1830s right up to the current period as illustrated in Figure 3. The quest for suitable refrigerants that are efficient, have low GWP, zero ODP and short atmospheric lifespan is still ongoing. The US National Institute of Standards and Technology (NIST) have until recently look into close to 60 million chemicals and found only 27 suitable efficient substance to replace R

410a. All 27 candidates are ‘slightly flammable’ (Rose 2017). Flammability is one of the concerns when hydrocarbons (HCs) are used in AC & R applications, and many parts of the world prohibit its use due to this inherent property.

Hydrocarbon Refrigerants

Greenpeace has categorised HC as one of the ‘gentle five’ which include carbon dioxide (R-744), water (R-718), air (R-729) and ammonia (R 717). The most commonly used HC refrigerants are ethane (R 170), propane (R-290), iso-butane (R-600a), and propylene (R-1270). HC refrigerants are categorised as A3 by ASHRAE *Standard 34* and *ISO 817* which means that these refrigerants are highly combustible with a lower flammability limit (LFL) of less or equal to 0.10kg m^{-3} and a heat of combustion of greater than or equal to $19,000\text{ kJ kg}^{-1}$. Table 1 shows some properties of four of the most commonly used HC refrigerants. Figure 4 shows HC refrigerants being marketed differently across different countries. Figure 4 (a) shows a white cylinder (U.S. Department of Transportation Standard 39 – Non-Refillable Cylinder) containing primarily of propane and is marketed as “HC 22a”, imported to Malaysia from the U.S.A. The photo in Figure 4 (b) shows an orange coloured cylinder which also contained propane being branded simply as “Refrigerant 290” and is imported from China. The material safety data sheets (MSDS) of both the HC refrigerants indicates that the contents are more than 98% propane.

Flammability of HCs when used as refrigerants, must be investigated in depth for its successful adoption as possible replacements to HCFC, HFC, and even HFO.

Figure 3. Development and progression of refrigerants (adapted from Calm 2008).

Table 1. Properties of Common HC Refrigerants (ASHRAE Handbook- Fundamentals 2013).

Refrigerant	Molecular mass M, (g mol ⁻¹)	Critical temperature, t _{cr} (°C)	Critical pressure, P _{cr} (MPa)	Boiling point, T _{bp} (°C)	Atmospheric Lifetime, Years	ODP	GWP
R 290	44.0	96.740	3.80	– 42.2	0.041	0	20
R 600a	58.1	134.660	3.64	– 0.5	0.016	0	20
R 1270	42.1	91.061	4.67	– 47.7	0.001	0	20
R 170	30.1	32.200	4.87	– 88.6	0.167	0	20

Figure 4. (a) Propane marketed as HC 22a (b) Propane marketed as refrigerant 290.

Flammability Issues and Classification of Hydrocarbon Refrigerants

Flammability qualities inherent with HC refrigerants is one of the major factors in preventing its extensive usage in ACR industries, despite its extremely low GWP values. However, it must be noted that for HC to combust, it must meet three conditions and these are firstly, HC and air mixture ratio, must be within its flammability ranges of lower flammability limit (LFL) and upper flammability limit (UFL), secondly ignition temperature must be high enough to start the combustion and finally, oxygen that air contains must be within the correct fuel/air mixture for combustion to occur. *Figure 5* shows the common typical 'Fire Triangle' requirements for combustion to happen. For HC refrigerants to combust, they must meet the demands of the Fire Triangle which are (1) The availability of oxygen as the oxidizer, (2) The ignition temperature and the fuel in the correct mixture. For propane to be able to combust, the proper ratio of propane and air is between 2% –10% of propane mixed with 98% – 90% of the air in the presence of an ignition source that reaches 493°C.

Figure 5. The Fire Triangle.

Due to this inherent factor, many researchers have conducted experiments on the flammability issues of HC refrigerants used in vapour compression cycles. Some have conducted using simulation with a number using actual equipment in test chambers.

Coulbourne and Suen (2003) simulated the leaking scenario of HCs in an enclosed chamber and concluded that smaller amount HCs is mixed with the surrounding air the safety aspects of using HC refrigerants will be enhanced. Coulbourne and Espersen (2013), using the quantitative risk assessment (QRA) technique have established that ignition frequencies (IF) in ice cream cabinets that uses R 290 placed in different room sizes and position to be in a range of 2×10^{-13} to about 1×10^{-8} per year as compared to a typical frequency of fire in household refrigerator of 1×10^{-5} per year. Coulbourne and Suen (2015) studied and evaluated the risk of split air conditioners and refrigerator using hydrocarbon refrigerants and concluded that ignition frequency (IF) of both refrigerators and split air conditioner being extremely small. In refrigerators, it was found that only one ignition event per million units of refrigerators in a 10 years period and in the split air conditioners, one event per 100 million of split air conditioners in 10 years was reported.

Li (2014), uses gas detectors set up at various locations to detect leaking R 290 from a split type air conditioner and established that in an enclosed room concentrations of leaking HC is around 1/3 of LFL and HC will reach LFL at a region directly below the indoor unit. Zhang *et al.* (2013), ignited leaking refrigerants from a split unit air conditioner in a controlled environment and established that R 290 will ignite within a very close range of the indoor unit and combustion of R 290 leaking in an enclosed space will create a pressure of 6.5 kPa above atmospheric pressure. There will be secondary smoke generated from the burning indoor unit.

Li *et al.* (2013) and Nagaosa (2014) conducted simulation with mathematical modelling and computational fluid dynamics (CFD) to ascertain the effects of leaking HC from a source in an enclosed space.

All the above was conducted to allay the fear of the flammable properties of the HC refrigerants. Someways can be employed by users of HC to avoid the incidents of explosions or fire from leaking HCs from air conditioning equipment. One of the methods that can ensure the safe use of HC refrigerants is to minimise the charge allowed into the air conditioner unit to levels well below the LFL. This can be done by establishing set of rules, regulations, and standards to minimise charge and adopt passive and active safety measures when using HC refrigerants.

Due to concerns on the flammability of HC refrigerants, standards and guides were already being developed and used as a basis to use these refrigerants safely. These standards and guides are comprehensive documents to allow HC refrigerants to be used in correct locations and amount of refrigerant allowed to be charged into a system.

Standards and Guides for Safe Operation of Hydrocarbon Refrigerants

Good and safe design can overcome flammability issues of HC refrigerants based on standards and safety guides that are widely available today. Some of the more popular adopted standards on refrigerants and in particular HC refrigerants are published by authoritative bodies that are involved with the AC&R industries and national standard bodies.

The American Society of Heating Refrigerating and Air Conditioning Engineers (ASHRAE), which has published several well adopted and authoritative standards which deal solely with the safe use of refrigerants and

include the following standards:

- (1) Standard 15, Safety Standard for Refrigeration Systems
- (2) Standard 34, Designation and Safety Classification of Refrigerants; and
- (3) Standard 147, Reducing the Release of Halogenated Refrigerants from Refrigerating and Air Conditioning Equipment.

Other than ASHRAE, the International Organisation for Standardization (ISO) also publishes standards that concern the safe use of refrigerants. The *ISO 5149: 2014* Refrigeration and Systems and Heat Pumps- Safety and Environmental Requirements which comprise three parts and are as follows:

- (1) Part 1 — Definitions, classification and selection criteria.
- (2) Part 2 — Design, construction, testing, marking and documentation; and
- (3) Part 3 — Installation site.

The *ISO 817:2014* is a standard that deals with ‘Refrigerants—Designation and Safety Classification’. On the issues of refrigerant flammability, the ASHRAE 34 and *ISO 817*, both have a similar use of the flammability and toxicity levels classifications, as shown in *Table 2*. These existing standards about to refrigerants safety and compatibility are available and widely adopted in most industrialised nations.

Apart from the American and international standards, the European Union (E.U) having actively promoting environmentally friendly policies have published the EN 378 which deals with “Refrigeration Systems and Heat Pumps—Safety and Environmental Requirements”. This

Table 2. Classification of refrigerant.

Classifications	Explanations
Class A	Refrigerants that have an occupational exposure limit (OEL) of 400 ppm or greater
Class B	Refrigerants that have an OEL of less than 400 ppm, where the numeral 1, 2 and 3 denotes the following:
Class 1	No flame propagation in air at 60°C and 101.325 kPa
Class 2	Exhibits flame propagation in air at 60°C and 101.3 kPa, lower flammability limit (LFL) greater than 0.10 kg/m ³ at 23°C and 101.3 kPa, and heat of combustion less than 19 000kJ/kg
Class 2L	Class 2 refrigerants may be classified as 2L if they exhibit maximum burning capacity of no more than 100 mm/s at 23°C and 101.325 kPa
Class 3	Exhibits flame propagation in air at 60°C and 101.325 kPa and lower flammability limits (LFL) less than or equal to 0.10 kg/m ³ at 23°C and 101.325 kPa or heat of combustion greater than or equal 19 000 kJ/kg

standard comprises four parts which are:

- (1) Part 1—Basic requirements, definitions, classification and selection criteria
- (2) Part 2—Design, construction, testing, marking and documentation
- (3) Part 3—Installation site and personal protection
- (4) Part 3—Operation, maintenance, repair and recovery

With the four parts of the EN 378, this standard is a much better and comprehensive which can ensure that the equipment which uses the refrigerant can be designed, installed, operated and maintained properly. It deals with flammable, toxic and high-pressure refrigerants currently being chosen as a replacement for the environmentally damaging substances.

Annex C is useful for the calculation of maximum charge allowable for the HC used

in various locations of the building. Under the subtitle, C.3.1 Annex C, factory-sealed refrigeration systems with less than 150 g of A2 and A3 (flammable refrigerants) have “no location classification constraints” which means that most household refrigerators having less than 150 g of HC refrigerants or blends could be placed anywhere in a building.

The maximum charge allowable for air conditioning, heat pump and refrigeration equipment that does not comply to the factory sealed and charge HC of 150 grams and below shall be according to the following equations (*ISO 5149-1:2014* and *EN 378-1:2013*). Maximum charge allowable in human occupied spaces is estimated through Equation (1).

$$M_{\max} = 2.5 \times LFL^{5/4} \times h_0 \times A^{1/2} \quad (1)$$

When the refrigerant charge is known or ascertained than the minimum allowable area

that the equipment is allowed to be installed in human occupied areas shall be determined using Equation (2).

$$A_{\min} = m^2 \times (2.5 \times LFL^{5/4} \times h_0)^2 \quad (2)$$

where, $M_{\max}$ = Allowable maximum charge in a room in kg
 m = Refrigerant charge amount in the system in kg
 $A_{\min}$ = Required room area in m^2
 A = Room area in m^2
 LFL = Lower Flammable Limit in $kg\ m^{-3}$
 h_0 = Height factor of appliance as shown in *Table 3*.

Table 3. Height factor of appliance.

Appliance installation	Height factor
Floor	0.6
Wall mounted	1.8
Window mounted	1.0
Ceiling mounted	2.2

Some of the useful guides published to ensure safe application of HC refrigerants are already available online and can be downloaded freely. One of the more useful one that provides much comprehensive guide to operate split unit air conditioners using HC refrigerants is published by German International Cooperation (Programme Proklima) on behalf of the Federal Ministry for the Environment, Nature Conservation and Nuclear Safety of the Federal Republic of Germany. This guide provides the information to convert existing split type air conditioners that use HCFC to HC refrigerants.

The British Refrigeration Association (BRA) have also published a ‘Guide to Flammable Refrigerants’ which contains

useful information for safe use of HC from regulations and code of practices, transportation, applications and design to procedures in servicing and training. (BRA 2012) The Australian Institute of Refrigeration Air conditioning and Heating (AIRAH), first published the ‘Refrigerant Selection Guide’ in August 1994, updated in 2003 which includes a section on HC refrigerant. In 2013, AIRAH published an industry safety guide dedicated solely to flammable refrigerants. The latest guide is fully comprehensive as it consisted legislation, safety and risk requirements, emergency planning, service and maintenance, training and even a dedicated chapter on proper storage of flammable refrigerants. (AIRAH 2013).

Guides and standards are used to ensure that minimal amount of HC refrigerant is charged into systems to minimise the occurrence of the mixture of HC and air meeting the LFL levels when HC leaks from the AC. Guides and standards do not provide the information needed to properly design systems that use HC efficiently. The use of HC refrigerants must be safe and efficient as inefficient HC systems contribute more CO₂ emissions than conventional HCFC or HFC refrigerants as 90% of emissions are from indirect emissions. The energy efficiency ratios or coefficient of performances of HC must be considered together with safety when designing and installing air conditioning or refrigeration systems that utilises HC refrigerants.

Performance of Hydrocarbon Refrigerants

The coefficient of Performance (COP) or Energy Efficiency Ratio (EER) is the description of the performance of the refrigeration cycle.

$$COP = \frac{\text{Useful refrigeration effect}}{\text{Net energy supplied by external sources}}$$

Apart from this, the compression ratios, mass flow rate and temperature glides of the HC refrigerants must be taken into consideration in evaluating the full comparative analysis of the HC refrigerants. (AIRAH 2003). An example would be the molecular mass of R 290 (propane) is about half of that of HCFC 22 to have similar refrigeration effect. *Table 1* is adopted from the 2013 ASHRAE Fundamentals Handbook compares the refrigerant performance per kilowatt of refrigeration based on theoretical calculations. It was stated that actual results might differ significantly if other factors such as compressor efficiency and transport properties are taken into consideration. However, *Table 4* shows the similarities in performances between

R 290 and R 22 except the net refrigeration effect of R 290 which is almost 77% higher than that of R 22 and compressor displacement of R 290 is 17% higher than R 22. The comparison between R 600a and R 134a it replaces netted comparable results, where R 600a has 82% higher net refrigerating effect as compared to R 134a. However, the compressor displacement of R 600a is also much higher to that of R 134a by 86%.

Current AC&R systems that use R 22 and R 134a as refrigerants must take into consideration of changes in charge volume and compressor displacement if R 290 and R 600a are used as replacement refrigerants.

Table 4. Comparative refrigerant between R 22 and R 290 and R 134a and R 600a performance per KW of refrigeration (based on evaporator of 7.2°C and condenser of 30°C for R22 and R 290 and evaporator of -6.7°C and condenser of 30°C for R 134a and R 600a).

Refrigerant number and chemical name	EP MPa	CP MPa	CR	NRE kj/kg	RC g/s	LC L/s	SV of SC m ³ /kg	CD L/s	PC kW	COP	CDT °C
R22 chlorodifluoromethane	0.626	1.192	1.9	171.0	5.85	0.0050	0.0377	0.2205	0.0918	10.885	40.3
R 290 propane	0.588	1.079	1.84	303.9	3.29	0.0068	0.0787	0.2580	0.0931	10.743	32.6
R 134a tetrafluoroethane	0.228	0.770	3.37	153.0	6.54	0.0055	0.0880	0.5745	0.1650	6.063	34.8
R 600a isobutane	0.123	0.405	3.29	278.0	3.60	0.0066	0.2984	1.0723	0.1620	6.171	30.0

EP-Evaporator Pressure, CP-Condenser Pressure, CR-Compression Ratio, NRE-Net Refrigerating Effect, RC-Refrigerant Circulated, LC-Liquid Circulated, SV- Specific Volume, SC- Suction Gas, CD- Compressor Displacement, PC- Power Consumption, COP- Coefficient of Performance, CDT- Compressor Discharge Temperature.

In actual experiments, numerous authors have reported different results in comparing HC refrigerants with HCFC and HFC refrigerants. Halimic *et al.* (2003) examined R 290 with R 12 and R 410a in refrigeration cycles. It was conclusive that R 290 had highest cooling capacity and COP of R 290 equals that of R 12. Al Amir and Joudi (2014) reported the highest COP for R 290 as compared to R 22, R 407c and R 410a in ambient temperature of between 35°C to 55°C. Devotta *et al.* (2005) tested a window type air conditioner according to Indian Standard 1391 which resulted in COP of R 290 higher than that of R22 in ranges of 2.8 – 7.9%. He *et al.* (2014) experimented using chest freezer concluded that COP of R 290 is lower by 1.8% as compared to R 134a. Hatamipour *et al.* (2014) uses blends of R 290/R 600a in mass ratio of 56:44% in a domestic refrigerator resulting in reduction of energy consumption of 5.34% as compared to R 134a. Hwang *et al.* (2006) researched R 290 with R 404 and R 410a, where results indicated R 290 had COP improvements between 4% – 12%. Jayaraj and Muraleedharan (2007), indicated that COP of R 290/ R 600 in ratio of 45.2/54.8% is 3.6% higher than R 134a. Kim *et al.* (1998), uses the Korean Standard 9305 to compare R 600a and R 12 in domestic refrigerator. COP of R 600a had 6% improvements over R 12. Teng *et al.* (2012) reported that COP of R 290 is higher than R 22 at 50% of R 22 charge. Wongwises and Chimres (2005) blended R 290/ R 600 at a rate of 60/40% in a domestic refrigerator which results in reduced energy consumption of 4.86% compared to R 134a. Yang *et al.* (2012) concluded that a 20% increase in compressor displacement will enhance the performance of split unit ACs.

d'Angelo *et al.* (2016) simulated the use of a mixture of R 290/ R 600a in a vapour

injection refrigeration system. The best COP for a simulated vapour injection refrigeration system is when 40 wt% of R 290 and 60 wt% of R 600a is used.

It is conclusive that HCs have better performance than HCFC and HFC refrigerants as HCs were the first to be used as refrigerant in the early 1900s and were replaced by the synthesised refrigerants to overcome the flammability issues of HCs. CFCs, HCFCs and HFCs were manufactured to mimic performances of natural refrigerants without the need to worry about toxicities and combustibility issues.

CONCLUSIONS

With the impending phaseout and phasedown of ozone depleting and global warming refrigerants, Malaysia listed as 'article 5' group of the Montreal Protocol agreements has started to impose a targeted reduction of HCFC in industries beginning of 2016. The AC&R industries were most affected in particular the residential air conditioners markets when the DOE of Malaysia has imposed restrictions on the manufacture, importation, and installation of domestic AC of 2.5 hp and below to use HCFC 22. Manufacturers and importers switched to HFC 410a as replacements for R 22. This proves to be a wrong move as GWP of R 410a is higher than R 22. Besides, components and oil used in the ACs are incompatible. R 410a had 50% higher operating pressures and uses polyolester oil (POE) as opposed to mineral oil in R 22. Further to this two significant incompatibilities R 410a is not the long-term solution and is touted as a "transitional" refrigerant until a suitable replacement is found. R 410a will be banned in the European Union in a couple of years (1January 2025) (EU Regulation No

517/2014). The recently concluded meeting of parties to the Montreal Protocol on 15 October 2016 in Kigali, Rwanda (Kigali Amendment) added HFC in the original Montreal Protocol list of banned substance and targeted to be phased down. The Kigali Amendment will enter into force on 1 January 2019 when it is ratified by at least 20 parties of the original Montreal Protocol (UNEP 2016).

Standards, guides, legislation, and equipment (ATEX certified components) are already available for a safe and efficient use of HC based AC&R equipment in developed countries. It is about time that legislation on the use of HC is enacted in Malaysia as to enhance its safe and efficient use in AC&R industries considering the widely available international and regional standards and guides available for the adoption of HC and other natural refrigerants.

Regarding of performance of HCs, many researchers had unanimously concluded on the improved performances of HC and its blends compared to HCFC and HFC. These results should further prove that HCs are the best option for the replacement for HCFC instead of HFCs.

REFERENCES

- Australian Institute of Refrigeration and Heating 2003, *Refrigeration selection guide*, AIRAH, West Melbourne, Victoria, Australia.
- Australian Institute of Refrigeration and Heating 2013, *Flammable refrigerants-industry guide*, AIRAH, West Melbourne, Victoria, Australia.
- American Society of Heating, Refrigerating and Air-Conditioning Engineers 2013, *Fundamentals handbook*, ASHRAE, Atlanta, GA, U.S.A.
- American Society of Heating, Refrigerating and Air-Conditioning Engineers 2013, *Standard 15*, ASHRAE, Atlanta, GA, U.S.A.
- American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc 2013, *Standard 34*, ASHRAE, Atlanta, GA, U.S.A.
- Babiloni, AM, Esbri, JN, Cervera, AB, Moles, F & Peris B 2015, 'Analysis based on EU Regulation No 517/2014 of new HFC/HFO mixtures as alternative of high GWP refrigerants in refrigeration and HVAC systems', *International Journal of Refrigeration*, vol. 52, pp. 21–31.
- British Refrigeration Association 2012, *Guide to flammable refrigerants, Issue 1*, October 2012, Federation of Environmental and Trade Association, Reading, U.K.
- B.S. ISO 817 2014, *Refrigerants—designation and safety classification, 3rd edn*, British Standards Institution, London, U.K.
- B.S. prEN 378 2014, *Refrigerant systems and heat pumps-safety and environmental requirements*, Part 1–4, British Standards Institution, London, U.K.
- B.S. ISO 5149 2014, *Refrigeration systems and heat pumps-safety and environmental requirements*, Parts 1–4, British Standards Institution, London, U.K.
- Calm, JM 2008, 'The next generation of refrigerants—historical review, considerations, and outlook', *International Journal of Refrigeration*, vol. 31, pp. 1123–1133.
- Calm, JM & Didion, DA 1998, 'Trade-Offs in Refrigeration Selection: Past, Present and Future', *International Journal of Refrigeration*, vol. 21, no. 4, pp. 308–321.

- Colbourne, D & Espersen, L 2013, 'Quantitative Risk assessment of R 290 in Ice Cream Cabinets', *International Journal of Refrigeration*, vol. 36, pp. 1208–1219.
- Colbourne, D & Suen, KO 2003, 'Equipment design and installation features to disperse refrigerant releases in rooms-Part 1: Experiments and Analysis', *International Journal of Refrigeration*, vol. 26, pp. 667–673.
- Colbourne, D & Suen, KO 2003, 'Equipment design and installation features to disperse refrigerant releases in rooms-part 2: determination of procedures', *International Journal of Refrigeration*, vol. 26, pp. 674–680.
- Colbourne, D & Suen, KO 2015, 'Comparative evaluation of risk of a split air conditioner and refrigerator using hydrocarbon refrigerants', *International Journal of Refrigeration*, vol. 59, pp. 295–303.
- d'Angelo, JVH, Aute, V & Rademacher, R 2016, 'Performance evaluation of a vapour injection refrigeration system using mixture refrigerant R290/R600a', *International Journal of Refrigeration*, vol. 65, pp. 194–208.
- Department of Environment (DOE) Malaysia, 2010, Consultative Workshop on "HCFC Phaseout Management Plan (HPMP) for Malaysia, 4 October." DOE Malaysia.
- Department of Environment (DOE) Malaysia, 2015, 'Letter on "Extension of time for the ban of manufacturing, assembling and importing of air conditioning equipment using HCFC with capacities of 2.5 horse power and below" ', 22 May, DOE Malaysia.
- Devotta, S, Padalkar, AS & Sane, NK 2005, 'Performance assessment of HC-290 as a drop- in substitute to HCFC-22 in a window air- conditioner', *International Journal of Refrigeration*, vol. 28, pp. 594–604.
- European Commission 2006, Directive 2006/40/EC of the European Parliament and of the Council of 17 May 2006 relating to emissions from air conditioning systems in motor vehicles and amending council directive 70/156/EEC, *Official Journal of the European Union*, 2006. L 161/12 of 14.6.2006.
- European Commission 2014, Regulation no. 517, /2014 of the European Parliament and of the Council of 16 April 2014 on fluorinated gases and repealing Regulation (EC) No. 842/2006, *Official Journal of the European Union*, 2014. L 150/195 of 20.5.2014.
- Halimic, E, Ross, D, Agnew, B, Anderson, A & Potts, I 2003, 'A Comparison of Operating Performance of Alternative Refrigerants', *Applied Thermal Engineering*, vol. 23, pp. 1441–1451.
- He, MG, Song, X Z, Liu, H & Zhang, Y 2014, 'Application of natural propane and propane/isobutane in large capacity chest freezer', *Applied Thermal Engineering*, vol. 70, pp. 732–736.
- Hwang, Y, Jin, DH & Rademacher, R 2007, 'Comparison of R-290 and two HFC blends for walk- in refrigeration systems', *International Journal of Refrigeration*, vol. 30, pp. 633–641.
- Joudi, KA & Al Amir, QR 2014, 'Experimental assessment of residential split type air conditioning systems using alternative refrigerants to R22 at high ambient temperature', *Energy Conversion and Management*, vol. 86, pp. 496–506.
- Kim, MH, Lim, BH & Chu, ES 1998, 'The performance analysis of a hydrocarbon

- refrigerant R-600a in a household refrigerator/freezer', *KSME International Journal*, vol. 12, no.4, pp. 753–760.
- Lorentzen, G 1995, 'The Use of natural refrigerant: a complete solution to the CFC/ HFC predicament', *International Journal of Refrigeration*, vol.18, no. 3, pp. 190–197.
- Lee, YS & Su, CC 2002, 'Experimental studies of isobutane (R-600a) as refrigerant in domestic refrigeration system', *Applied Thermal Engineering*, vol. 22, pp. 507–519.
- Li, T 2014, 'Indoor leakage test for safety of R290 split type room air- conditioner', *International Journal of Refrigeration*, vol. 40, pp. 380–389.
- Li, YN, Tao, JJ, Han, YC, Han, X & Qin, J 2014, 'Numerical and experimental study on the diffusion property of difluoromethane (HFC 32) in leakage', in *Procedia Engineering*, vol. 71, pp. 34–43.
- Li, Q, Zhang, HM., Liu, Y., Huang, H, Zhang, X, Li, Z & Yao, W 2013, 'Influencing factors of flammable refrigerants leaking in building air- conditioning system', *Procedia Engineering*, vol. 62, pp. 648–654.
- Mohanraj, M., Jayaraj, S & Muraleedharan, C 2007, ' Improved energy efficiency for HFC134a domestic refrigerator retrofitted with hydrocarbon mixture (HC290/HC600a) as drop-in substitute', *Energy for Sustainable Development*, vol. 11, No. 4, pp. 29–33.
- Nagaosa, RS 2014, 'A new numerical formulation of gas leakage and spread into a residential space in terms of hazard analysis', *Journal of Hazardous Materials*, vol. 271, pp. 266–274.
- Rajadhyaksha,D, Wadia, BJ, Acharekar, AA & Colbourne. D 2015, 'The first 100 000 HC-290 split air conditioners in India', *International Journal of Refrigeration*, vol. 60, pp. 289–296.
- Rasti, M, Hatamipour, MS, Aghamiri, SF & Tavakoli, M 2012, 'Enhancement of domestic refrigerator's energy efficiency index using a hydrocarbon mixture refrigerant', *Measurement*, vol. 45, pp. 1807–1813.
- Rose, E 2017, 'Cold cas', *CIBSE Journal*, May 2017, pp. 39–43
- Teng, PT, Mo, HE, Lin, H, Tseng, YH, Liu, RH & Long, YF 2012, 'Retrofit assessment of window air-conditioner', *Applied Thermal Engineering*, vol. 32, pp. 100–107.
- UNEP 2016, 'Frequently asked questions relating to the Kigali Amendment to the Montreal Protocol ', Viewed 3 April 2017, <http://ec.europa.eu/clima/sites/clima/files/faq_kigali-amendment_en.pdf>
- U.S, EPA 2015, 'Significant new alternative policy (SNAP) report', viewed 26 September 2016, <<http://www.epa.gov/ozone/snap/index.html>>.
- Wongwises, S & Chimres, N 2005, 'Experimental study of hydrocarbon mixtures to replace HFC 134a in a domestic refrigerator', *Energy Conversion and Management*, vol. 46, pp. 85–100.
- Wu, JH, Yang, LD & Hou, L 2012, 'Experimental performance study of a small wall room air- conditioner retrofitted with R-290 and R-1270', *International Journal of Refrigeration*, vol. 35, pp. 1860–1868.
- Zhang, W, Yang, Z, Li, J, Ren, CX, Lu, D, Wang, J & Wu, W 2013, 'Research on the flammability hazards of an air – conditioner using refrigerant R-290', *International Journal of Refrigeration*, vol. 36, pp. 1483–1494.