AMMONIA AND PROPANE AS NATURAL REFRIGERANTS FOR HEAT PUMP APPLICATIONS

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ABSTRACT

Interest in the use of natural refrigerants in to minimize the environmental impact of air conditioning and refrigeration equipment is gaining strength. This article focuses on the performance of two candidate natural refrigerants: ammonia and propane for heat pump applications. Cycle configurations include: (1) basic vapor compression, (2) two configurations with different liquid-line/suction-line heat exchanger arrangements, and (3) a two-stage flash economizer cycle for evaluation of ammonia and propane in comparison to R-134a and R410A. The objective is to evaluate the relative performances of current and natural refrigerants and gauge which class is better suited to address the global energy and environmental challenges.

Keywords: Heat pump, Ammonia, Propane, COP, Entropy, natural refrigerants

1. INTRODUCTION

During last few decades, the ozone depleting potential (ODP) and global warming potential (GWP) have emerged as dominant characteristics for the development of new refrigerants to displace the conventional chloro-fluorocarbons (CFCs) and hydro-chloro-fluorocarbons (HCFCs) refrigerants. These conventional refrigerants have relatively high ODP and GWP and consequently are not environmental friendly. The advent of hydro-fluorocarbons (HFCs) started the gradual phase out of CFCs and HCFCs because HFCs have zero ODP although their GWP is still comparable to their predecessors (Table 1). The ultimate research goal is to find substitute refrigerants with zero ODP and zero GWP that can serve practical applications in the residential, commercial and industrial sectors. In this regard, the natural refrigerants offer some tangible advantages. This paper examines the performance of two natural refrigerants, ammonia and propane, and compares them to the widely used R134a and R410a in four heat pump cycles.

Table 1: Characteristics and environmental impact of different refrigerants (ASHRAE 2013)

Refrigerant group	Refrigerant example	ODP	GWP_{100}	Atmospheric lifetime (years)	Flammability
CFCs	R11, R12, R115	0.6–1	4750–14400	45–1700	Nonflammable
HCFCs	R22, R141b, R124	0.02–0.11	400–1800	1–20	Nonflammable
HFCs	R407C, R32, R134a	0	140–11700	1–300	Nonflammable or mildly flammable
HFOs	R1234fy, R1234ze, R1234yz	0	0–12	-	Mildly flammable
Natural refrigerants	R744, R717, HC (R290, R600, R600a)	0	0	Few days	HCs: Highly flammable R717: Flammable R744: Nonflammable

Despite their unfavorable flammability characteristics (classified as A3), HCs appear promising in preliminary assessment studies. They have zero ODP, very low GWP, and are also non-toxic. Additionally, they show high miscibility with mineral oil and compatibility with various compressors.

Several, analytical, and numerical studies have evaluated the performance of HCs for various HVAC&R applications. Broadly, these refrigerant studies used either pure HCs, HC blends, or HC blends mixed with HFCs and hydrofluoroolefins (HFOs). Many investigations have been conducted in the research into substitutes for CFC12 and CFC22. Wongwises et al. (2006) conducted an experimental study on the application of hydrocarbon mixtures to replace HFC134a in automotive air conditioners. The hydrocarbons investigated included propane (R290), butane (R600), and isobutane (R600a). In another study Wongwises and Chimres (2005) evaluated the performance of a mixture of propane, butane, and isobutene to replace HFC134a in a domestic refrigerator. Jung et al. (1999) evaluated the performance of a propane/isobutane (R290/ R600a) mixture to determine their performance for domestic refrigerators. Granryd (2001) evaluated the possibilities and problems of using hydrocarbons as working fluids in refrigeration equipment. Park et al. (2010) conducted an experimental study using two pure hydrocarbons and seven mixtures composed of propylene, propane, HFC152a, and dimethylether as an alternative to HCFC22 in residential air-conditioners and heat pumps. Urchueguia et al. (2004) conducted an experimental study of a commercial refrigeration unit using R290 instead of R22. They concluded that the COP increased by 1–3% and the capacity decreased by 13–20% when R290 was used to replace R22. In another similar study Halimic et al. (2003) evaluated R290 as a substitute for R12 in a traditional refrigeration system and found that the capacity of R290 was higher than the refrigerant R12 and the other refrigerants included in the study. Lee and Su (2002) compared the performance of a domestic refrigeration system with R600a to replace R12 and R22. El-Morsi (2015) conducted an analytical study to compare the energetic and exergetic performance of a domestic refrigeration unit using R290, R600, and R134a and concluded that R600 had superior performance compared to R290 and R134a. Khalid and Qusay (2014) investigated the performance of a residential air-conditioning system under high condensing temperatures using R22, R290, R407C, and R410A.

Similar to HCs, ammonia is a natural refrigerant with ODP and GWP equal to zero. Compared to conventional refrigerants it has inherently high refrigeration capacity per unit mass, excellent thermodynamic properties, and high heat transfer coefficients (Ayub, 2010). The primary disadvantage of ammonia is its toxic effect at concentrations above 300 ppm; however, this risk is somewhat mitigated by its pungent smell alerting humans of its presence. Even at low concentrations ~ 5 ppm, olfactory senses can detect the distinct smell of this gas.. Ammonia is classified as, “moderately flammable” in air when its concentration ranges between 16-28 wt. %, and it is not compatible with copper and copper alloys. Ammonia has been used in refrigeration application for over 100 years and there are multiple studies supporting its use for small and large refrigeration applications (Ayub and Ayub, 2015). Similarly, there has been extensive effort to investigate the performance of the fluid in thermally driven heat pump systems (absorption systems etc.) (Darwish et al., 2008; Acuña et al., 2013; Rivera et al., 2007). However rare information is available for the use of ammonia as a refrigerant in an air-conditioning or heat pump application.

Overall it can be concluded from published literature that most of the studies have focused on evaluating the natural refrigerants specifically propane and ammonia, mainly as a drop-in-replacement option. These studies have been straight forward experiments, or simple First Law based thermodynamic analysis. For HCs studies have focused both on refrigeration and heat pumps (vapor compression systems), while for ammonia the focus has been mainly on refrigeration and thermally driven systems. Although these studies have provided valuable information regarding which refrigerant might suitably replace R134a or R410, the full impact of the replacement requires more work. More specifically, there has been no information about what is the energy and exergy impacts of natural refrigerants compared to existing fluids. The current study examines this issue on the basis of the First and Second Laws of thermodynamics and looks at the impact of each component in the cycle to identify sources of systemic inefficiency. We present the performance of two natural, and two widely used refrigerants in the four heat pump cycles mentioned above.

2. DEVELOPMENT OF MODEL FOR PERFORMANCE COMPARISON

The analysis was conducted by applying energy balances, entropy generation, and availability analysis to the various configurations to quantify the performance. The energy balance from the First Law of thermodynamics is expressed by Equation (1) (Warke, 1995):

$$\sum \dot{Q}_{cv} + \dot{W}_{cv} + \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right) - \sum_{out} \dot{m}\left(h + \frac{V^2}{2} + gz\right) = \frac{dE_{cv}}{dt} = \frac{d}{dt}\left[m\left(u + \frac{V^2}{2} + gz\right)\right] \quad (1)$$

The general entropy production equation is

$$\frac{dS_{cv}}{dt} + \sum_{out} \dot{m}(s) - \sum_{in} \dot{m}(s) = \sum \frac{\dot{Q}_{cv}}{T} + \dot{\sigma}_{cv} \quad (2)$$

Since the First Law Equation (1) contains a work term but no entropy terms, and the Second Law Equation contains entropy terms but no work term, it is useful to combine the two to yield:

$$\dot{W}_{cv} = \sum_{out} \dot{m}\left(h - T_o s + \frac{V^2}{2} + gz\right) - \sum_{in} \dot{m}\left(h - T_o s + \frac{V^2}{2} + gz\right) - \sum_j \dot{Q}_j\left(1 - \frac{T_o}{T_j}\right) + \frac{dE_{cv}}{dt} - T_o\left[\frac{dS_{cv}}{dt} - \dot{\sigma}_{total}\right] \quad (3)$$

where T_o is the reference temperature taken to be 273.15 K; Q_j is the heat transfer at the control surface to or from thermal reservoirs at T_o or T_j; S_{cv} is the entropy within the control volume; and σ_{cv} is the total rate of entropy generation. Under steady-state conditions, Equation (1) is reduced to

$$\sum \dot{Q}_{cv} + \dot{W}_{cv} + \sum_{in} \dot{m}\left(h + \frac{V^2}{2} + gz\right) - \sum_{out} \dot{m}\left(h + \frac{V^2}{2} + gz\right) = 0 \quad (4)$$

and under steady-state and no-flow conditions, Equations 2 and 3 reduce to

$$\dot{\sigma}_{cv} = -\sum_j \frac{\dot{Q}_j}{T_j} \quad (5)$$

and

$$\dot{W}_{cv,actual} = -\sum_j \dot{Q}_j\left(1 - \frac{T_o}{T_j}\right) + T_o\dot{\sigma}_{cv} \quad (6)$$

With $\dot{I}_{cv} = T_o\dot{\sigma}_{cv}$

The minimum steady-state, no-flow rate of work, W_{cv} is when the entropy generation term is zero:

$$\dot{W}_{cv,\min} = -\sum_j \dot{Q}_j\left(1 - \frac{T_o}{T_j}\right) \quad (7)$$

In order the evaluate the performance of various working fluids a program was written using the Engineering Equation Solver (EES) for each cycle configuration. Figure 1 through 4 present the schematics for various cycles:

- i- Configuration 1 is a modified vapor compression cycle where a heat exchanger is installed to exchange the heat between suction line and liquid line.
- ii- Configuration 2 presents a system where the vapor liquid mixture at the exit of evaporator is routed through the condenser to reach the saturated vapor state before entering the compressor.
- iii- Configuration 3 is a simple vapor compression cycle consisting of four major components.
- iv- Configuration 4 is the configuration consisting of flash tank installed between two expansion valves. The flash tank, low-pressure compressor and high-pressure compressor are connected through a mixing chamber.

For all configurations the evaporating temperature of 10 °C and condensing temperature of 40 °C is fixed, along with the ideal assumptions of zero pressure drop in the heat exchangers and a 100% efficient compression process. These assumptions are justifiable for a preliminary analysis without the complication of equipment specifications and compressor maps.

For configuration 2 and 3, the vapor quality at the exit of the evaporator was fixed at 90% which meant that in order to enter the compressor as saturated vapor, additional heat was supplied through LL/SL-HX and the condenser for configuration 2 and 3, respectivley. For configuration 4, a fixed compression ratio was assumed between the two compressors, and the high-side pressure for all cycles was fixed according to the condensing temperature (40°C).

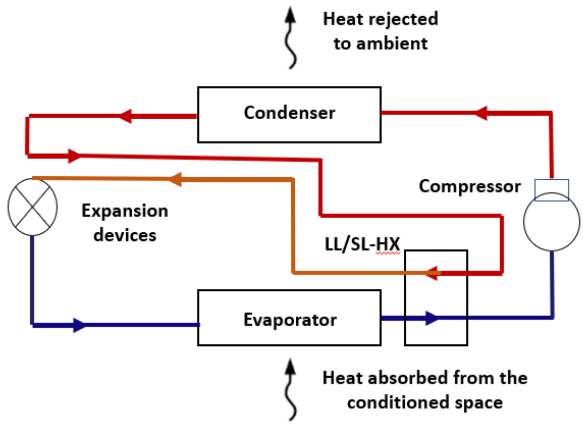

Figure 1: Configuration 1 (Vapor compression cycle with LL/SL-HX)

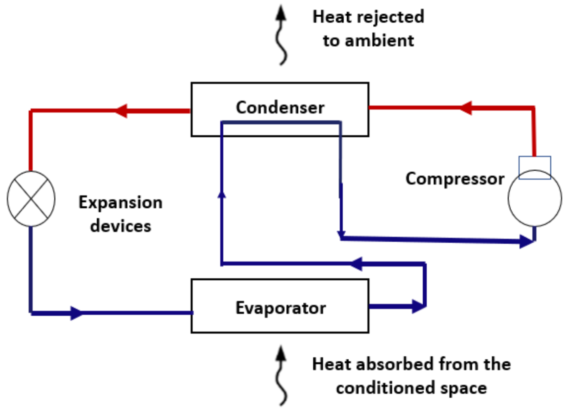

Figure 2: Configuration 2 (Vapor compression cycle with LL/SL-HX combined condenser)

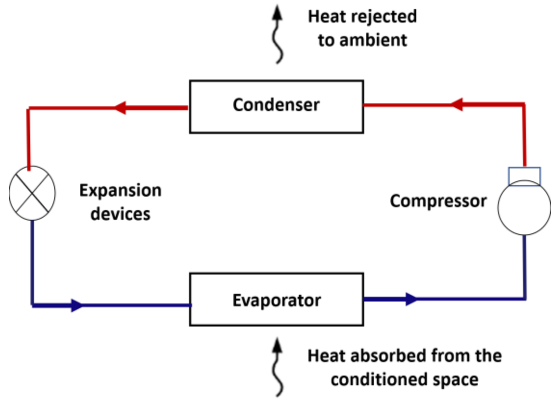

Figure 3: Configuration 3 (simple vapor compression

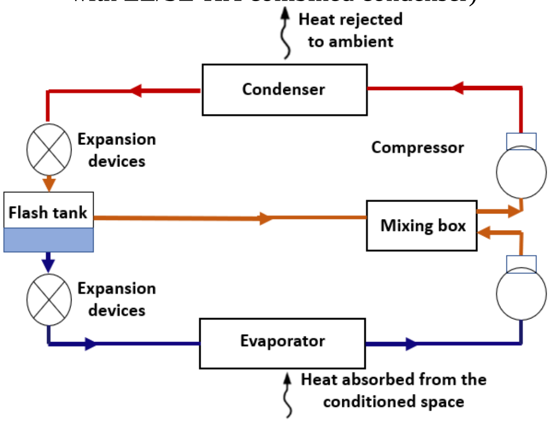

Figure 4: Configuration 4 (Vapor compression cycle with flash tank)

3. FIRST LAW ANALYSIS OF VARIOUS CONFIGURATIONS

The first law analysis has been conducted with the objective of estimating the COP of various refrigerants when they are deployed in selected configurations. Tables 2 through 5 present the heat duty, refrigerant flow rates, and COP relative to the Carnot COP as well as the COP normalized to ammonia. Thus the interpretation of the COP values are relative to that of ammonia. (column 7 in the respective Tables). It can be observed that ammonia based systems have the highest COP for all the cases. $Q_{vol.}$ is a parameter that influences equipment size, with larger values of corresponding to smaller systems. In this regard, on a relative basis, ammonia has the highest Q_{vol} representing the most compact system (Fig. 5).

Mass flow rate is another important parameter. Based on our analysis, ammonia requires the least mass flow rate among the selected refrigerant. This can be attributed to higher heat of vaporization of the fluid relative to the other refrigerants. While the low mass flow rate confirms the lower compressor power, it can be related to the required refrigerant charge in the system. However, a more direct parameter of interest in this regard is the volumetric capacity which establishes the compressor size. Interestingly, ammonia has the highest volumetric capacity when compared to the other fluids. Based on relative COP and Qvol values ammonia based system will be not only more efficient but will also be more compact when compared to R134a and R410A based systems. The findings are summarized in Figure. 5 where the relative volumetric capacity has been plotted against the relative COP (with respect to ammonia for each of the four configurations).

Although propane, does not show a promising COP when compared to ammonia or R410a, it's COP is better compared to R134a for all the configuration considered in the study. This is an important observation as it indicates that propane may be a reasonably good drop-in-replacement for R-134a. Another observation is the mass flow rate. For all the cases considered, the relative mass flow rate for propane is almost half compared to R134a and R410 based systems. This leads to less compressor power consumption. Furthermore, the volumetric capacity of propane is higher compared to R134a attributable to a higher heat of vaporization of propane. A more compact system also requires less refrigerant charge. Lower refrigerant mass for ammonia and propane is a critical advantage since both fluids are classified as flammable (ammonia is A2L: mildly flammable and propane is A3: flammable).

Table 2: Performance of various refrigerants for configuration 1

Refrigerants	Q_evap	Q_evap/m	m_evp	Vol. Cap.	COP/COP_{Carnot}	COP/COPCarnot relative to NH_3	VolCap relative to NH_3
	kW	$kJ \cdot kg^{-1}$	$kg \cdot s^{-1}$	$MJ \cdot m^{-3}$			
Ammonia	174.779	907	0.1927	3.136238	0.2406	1.000	1.000
R134a	174.874	101.2	1.728	1.461372	0.2039	0.848	0.466
R290	174.789	186.9	0.9352	1.936587	0.1966	0.817	0.617
R410a	174.924	101.7	1.72	3.109141	0.1720	0.715	0.991

Table 3: Performance of various refrigerants for configuration 2

Refrigerants	Q_evap	Q_evap/m	m_evp	Vol. Cap.	COP/COP_{Carnot}	COP/COPCarnot relative to NH3	VolCap relative to NH3
Ammonia	174.779	907	0.1927	3.136238	0.2406	1.000	1.000
R134a	174.874	101.2	1.728	1.461372	0.2039	0.848	0.466
R290	174.789	186.9	0.9352	1.936587	0.1966	0.817	0.617
R410a	174.924	101.7	1.72	3.109141	0.1714	0.712	0.991

Table 4: Performance of various refrigerants for configuration 3

Refrigerants	Q_evap	Q_evap/m	m_evp	Vol. Cap.	COP/COP_{Carnot}	COP/COPCarnot relative to NH3	VolCap relative to NH3
Ammonia	174.812	970.1	0.1802	3.354426	0.2573	1.000	1.000
R134a	174.760	111.1	1.573	1.604332	0.2241	0.871	0.478
R290	174.845	205.7	0.85	2.131385	0.2164	0.841	0.635
R410a	174.798	112.7	1.551	3.44543	0.1901	0.739	1.027

Table 5: Performance of various refrigerants for configuration 4

Refrigerants	Q_evap	Q_evap/m	m_evp	m_cond	Vol. Cap.	COP/COP_{Carnot}	COP/COPCarnot relative to NH3	VolCap relative to NH3
Ammonia	174.830	1136	0.1539	0.1796	10.87132	0.6401136	1.000	1.000
R134a	174.824	161.5	1.0825	1.5163	6.212853	0.349798315	0.546	0.571
R290	174.822	303.6	0.57583	0.81705	7.731457	0.34216601	0.535	0.711

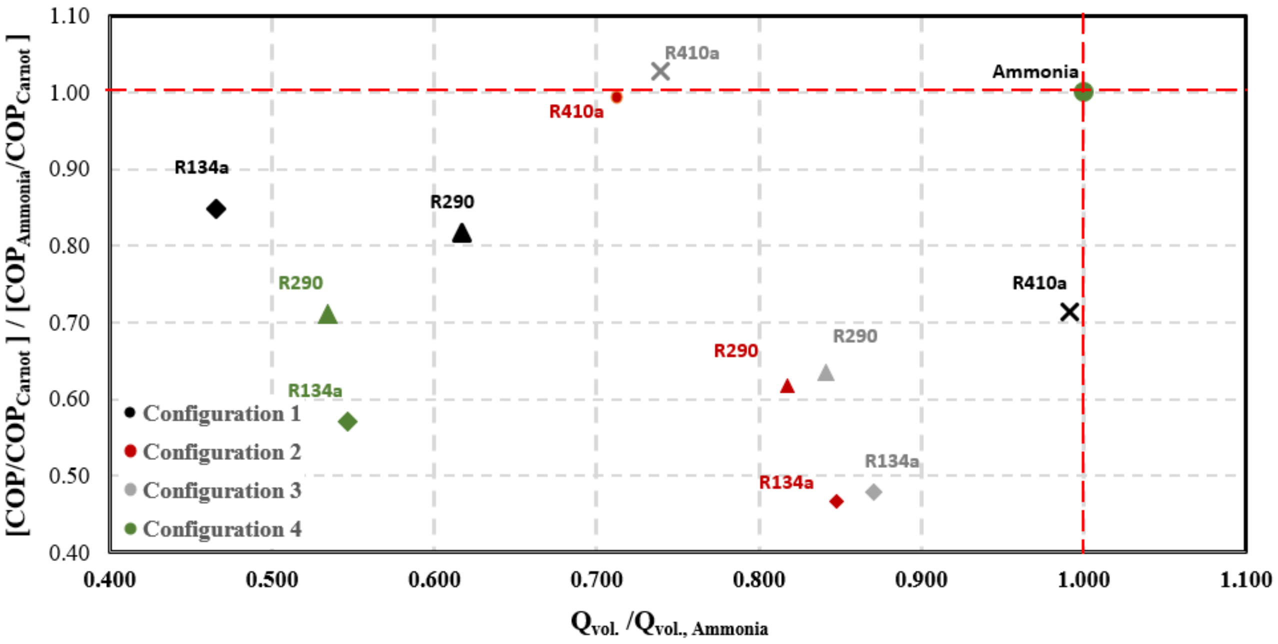

Figure 5: COP and Volumetric Efficiency of Select Refrigerants Relative to Ammonia

4. SECOND LAW ANALYSIS OF VARIOUS CONFIGURATIONS

The Second Law of thermodynamics is used to evaluate the irreversibility for individual components of various configurations for each refrigerant. Table 6 through 9 summarizes components-wise and total irreversibility for each configuration and for each fluid. It is observed that ammonia has the lowest total irreversibility and like the other fluids, the maximum irreversibility occurs in the condenser. It is important to distinguish between the parameters in the last two columns. The second last column presents irreversibility per unit mass flow rate while the last column presents the total irreversibility. Interestingly, the total irreversibility per unit mass flow rate is highest for the ammonia as working fluid for all configurations. However, due to the relatively smaller mass flow rate in the case of ammonia, the overall irreversibility is the smallest. When the respective values are compared for R290, the pattern is similar.

Table 6: Component's irreversibility for various refrigerants for configuration 1

Configuration 1		Compressor	condenser	Intercooler	EXV	Evaporator	Total Irreversibility	
		(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	kW
	AMMONIA	0.00	162.93	12.21	34.01	0.23	209.38	40.35
	R134a	0.00	16.60	2.03	10.41	0.05	29.09	50.27
	R290	0.00	30.87	3.91	21.40	-0.07	56.12	52.48
	R410a	0.00	18.65	2.35	14.95	-0.09	35.86	61.68

Table 7: Component's irreversibility for various refrigerants for configuration 2

Configuration 2		Compressor	condenser	EXV	Evaporator	Total Irreversibility	
		(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	kW
	AMMONIA	0.00	175.34	34.01	0.25	209.60	40.39
	R134a	0.00	18.44	10.41	0.05	28.90	49.93
	R290	0.00	34.57	21.32	0.02	55.92	52.29
	R410a	0.00	21.00	14.95	0.01	35.96	61.85

Table 8: Component's irreversibility for various refrigerants for configuration 3

Configuration 3		Compressor	condenser	EXV	Evaporator	Total Irreversibility	
		(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	kW
	AMMONIA	0.00	170.63	34.01	0.35	204.98	36.94
	R134a	0.00	17.77	10.41	0	28.18	44.32
	R290	0.00	33.16	21.40	0	54.56	46.37
	R410a	0.00	20.08	14.95	0.12	35.15	54.51

Table 9: Component's irreversibility for various refrigerants for configuration 4

Configuration 4		condenser	EXV 1	Flash Tank	EXV 2	Mixer	Evaporator	Total Irreversibility
		(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kJ·kg^{-1}·K^{-1})	(kW)
	AMMONIA	23.02808	10.993125	0.0048676	7.27012	0.660689	0	41.96
	R134a	15.23846	3.40054	0.0067113	2.198625	-0.003510	0	20.83
	R290	28.43820	7.27012	0.009360	4.661085	0.012808	0.01691	40.39

Figure 6. compares the total irreversibility of selected refrigerants in different configurations. It is observed that systemic irreversibility is configuration dependent. Irreversibility associated with thermal transfers, expansion, compression etc. vary based on the configuration. Overall, ammonia has the least irreversibility for all configurations expect for configuration 4 where R134a has the best performance. Interestingly, R410A has the highest irreversibility for all the proposed configuration. Configuration 4 has been skipped form analysis for R410A since the glide nature of the refrigerant precluded a proper accounting of the flash tank state points.

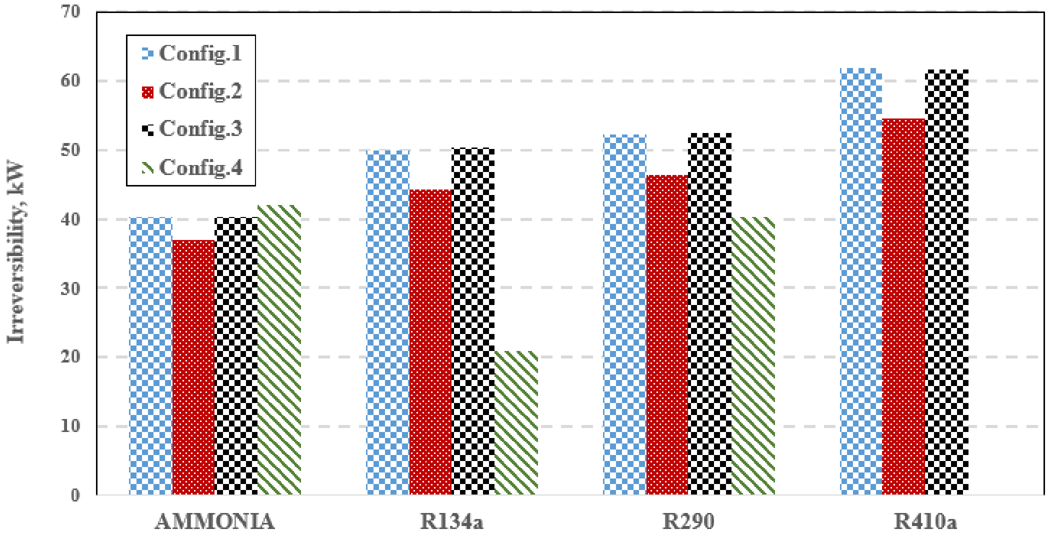

Figure 6: Total irreversibility for Select Refrigerants for various configurations

4. CONCLUSIONS

Both natural refrigerants (propane and ammonia) can potentially replace R134a and R410A refrigerants in a heat pump application. For the simplest configuration (3) ammonia outperforms (least irreversibility) the other three refrigerants. It can be inferred that ammonia has the least total irreversibility except for configuration 4 where R134a has noticeably lower irreversibility. Overall, both propane and ammonia alternative refrigerants show satisfactory performance as replacement candidates for R134a and R410A. Ammonia represents the most compact design because of its high volumetric capacity. In all four configurations, ammonia has the lowest mass flow rate. Among all four cycles, the simplest one (configuration 3) is the recommended choice.

ACKNOWLEDGEMENTS

Funding for this work is provided by the US Department of Energy, Washington, DC. The authors thank Mr. Antonio Bouza, program manager for the DOE Office of Building Technologies, for his full support.

NOMENCLATURE

E	Energy (J)	I	Irreversibility (W/K)
T	Temperature (K)	S	Entropy (W/K)
Q	Heat transfer rate (Watts)	z	Height (m)
W	Work rate (Watts)	m	Mass (kg)
h	Enthalpy (W/m^2-K)	$\dot{\sigma}$	Entropy generation rate (W/K-sec)
V	Velocity (m/s)	u	Internal Energy (W)
g	Acceleration due to gravity (m/s^2)	COP	Coefficient of performance

REFERENCES

Acuña, A., Velázquez, N., Cerezo, J., 2013, Energy analysis of a diffusion absorption cooling system using lithium nitrate, sodium thiocyanate and water as absorbent substances and ammonia as the refrigerant Applied Thermal Engineering, 51, 1273-1281

ANSI/ASHRAE STANDARD 34, Designation and Safety Classification of Refrigerants, 2013.

Darwish, N. A., Al-Hashimi, S. H., Al-Mansoori, A. S., 2008, Performance analysis and evaluation of a commercial absorption–refrigeration water–ammonia (ARWA) system, Internacional Journal of Refrigeration, 31, 1214-1223.

El-Morsi, M., 2015. Energy and exergy analysis of LPG (liquefied petroleum gas) as a drop-in replacement for R134a in domestic refrigerators, Energy, 86, 344–53.

Granryd, E., 2001. Hydrocarbons – an overview, International Journal of Refrigeration, 24, 15–24.

Halimic, E., Ross, D., Agnew, B., Anderson, A., Potts, I. A, 2003. comparison of the operating performance of alternative refrigerants, Applied Thermal Engineering, 23, 1441–51.

Jung, D., Park, B., Lee, H., 1999. Evaluation of supplementary/retrofit refrigerants for automobile air-conditioners charged with CFC12, International Journal Refrigeration, 22, 558–68.

Khalid, A. J., Qusay, R. A., 2014. Experimental assessment of residential split type air-conditioning systems using alternative refrigerants to R-22 at high ambient temperatures. Energy Conversion Management, 86:496–506.

Lee, Y. S., Su, C. C., 2002. Experimental studies of isobutane (R600a) as the refrigerant in domestic refrigeration system, Applied Thermal Engineering, 22, 507–19.

Park, K. J., Shim, Y. B., Jung, D., 2010. Performance of R170/R1270 mixture under air conditioning and heat pumping conditions, Journal of Mechanical Science and Technology, 24,879–85.

Rivera, C., Pilatowsky, I., Méndez, E., Rivera, W., 2007, Experimental study of a thermo-chemical refrigerator using the barium chloride–ammonia reaction, International Journal of Hydrogen Energy, 2007, 32, 3154-3158

Urchueguıa, J. F., Corberan, J. M., Gonzalvez, J., Dıaz, J. M., 2004. Experimental characterization of a commercial-size scroll and reciprocating compressor working with R22 and propane (R290) as refrigerant. Ecolibrium, 23–5.

Wongwises, S., Chimres, N., 2005. Experimental study of hydrocarbon mixtures to replace HFC-134a in domestic refrigerator. Energy Conversation Management, 46, 85–100.

Wongwises, S., Kamboon, A., Orachon, B., 2006. Experimental investigation of hydrocarbon mixtures to replace HFC-134a in an automotive air conditioning system. Energy Conversion Management, 47, 1644–59.

Z. H. Ayub, and A. H. Ayub. 2015. Replacing Two Shell and Plate Exchangers with a Single Special Design Shell and Tube Ammonia Flooded Evaporator at a Major Food Plant—A Case Study. *Heat Transfer Engineering* 37 1075-1078.

Zahid Ayub, 2010, Status of enhanced heat transfer in systems with natural refrigerants, Journal of Thermal Science and Engineering Applications, 2(4), 044001.