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REVIEW

A Historical Review on the Tribological Performance of Refrigerants used in Compressors

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A B S T R A C T

Refrigerants directly affect the tribological performance of interacting components in a compressor. Since the introduction of artificially formulated refrigerants, the types of refrigerants used in compressors have changed over the years. Apart from evaluating the physical, chemical and thermodynamic properties of refrigerants, the refrigerants have also been studied from a view point of tribology by various researchers worldwide. Changing a refrigerant in a compressor not only has an effect on the thermodynamic cycle but also effects the lubricants viscosity, lubricants pressure-viscosity coefficient, oil film thickness, lubricant/refrigerant miscibility, friction, wear, durability, reliability and overall power consumption. Refrigerants have been studied from a view point of tribology by varying the contact geometries, by using different lubricating oils with and without additives, by altering the environmental pressure/temperature, by changing the phase of the refrigerant, by using different interacting materials and by applying numerous surface treatments. The tribological behavior of refrigerants can be better understood by consolidating the findings in a comprehensive manner. An in-depth review on the tribological behavior of refrigerants is missing from the literature. This article reviews the tribological studies carried out on refrigerants, with focus on refrigerants used in domestic appliances, automobile air-conditioning systems and small scale industrial and commercial applications.

1. INTRODUCTION

Use of refrigerants dates back to ancient times where water vaporization and other evaporation processes were used as a means of cooling. A system that used a volatile fluid to produce ice in a closed cycle was first described by Oliver Evans. The proposed system which has no record of being actually built, used ether as a refrigerant under vacuum. Ether was to be evaporated under vacuum and the vapors were to be pumped to a water cooled heat exchanger to condense for reuse. Perkins probably influenced by this idea built the first working machine that used mechanical vapor-compression cycle. Perkins patent describes the use of a volatile fluid for the purpose of cooling/freezing, and at the same time condensing the fluid for reuse without waste.

Compounds such as Sulfur Dioxide (R-764), Ammonia (R-717), Methyl Chloride (R-40) and Methyl Formate (R-611) were being used as refrigerants before the 1930s but, their high toxicity and flammability reduced their potential of being used on a global scale in domestic cooling and refrigeration systems. Several fatal accidents occurred in the 1920s because of methyl chloride leakage from refrigerators. This started a collaborative research in 1928 for a refrigerant replacement that would be nontoxic and nonflammable by Frigidaire, DuPont and General Motors Research Corporation. This collaborative research led to the development of Dichlorodifluoromethane (CFC-12), Trichlorofluoromethane (CFC-11), Chlorodifluoromethane (HCFC-22), Trichlorotrifluoroethane (CFC-113), and Dichlorotetrafluoroethane (CFC-114). Commercial production of CFC-12 started in 1931. Chlorofluorocarbons (CFCs) and Hydrochlorofluorocarbons (HCFCs) possessed excellent thermodynamic properties as refrigerants besides being nonflammable and nontoxic. This made them the ideal refrigerants of their time, especially for use in small commercial, automotive and residential refrigeration applications.

Tribological studies of CFCs and HCFCs have also been carried out by various researchers to evaluate their mechanical, friction and wear properties. The lubrication conditions in a rolling piston type rotary compressor using HCFC-22 were investigated by [1]. The study focused on the friction and wear behavior of journal bearings and the vane-tip using ferrous and nonferrous metals. Focusing on CFCs; the viscosity, density and miscibility of various refrigerants in oils for use in refrigerator compressors was discussed by [2]. These factors affect the lubrication regime in a compressor which influences the friction coefficient and the amount of wear. Lubrication film thickness is a function of physical parameters including the lubricants viscosity and pressure-viscosity coefficient. The lubrication film dictates the wear in interacting parts and components. Viscosity and the pressure-viscosity coefficient for roller bearings element used in screw compressors were experimentally investigated by using oil-rich solution of naphthenic oil and HCFC-22 as refrigerant [3]. The results showed that viscosity of the oil dropped sharply after charging the refrigerant and then slowly increased until the solution reached an equilibrium value. Tribological assessment of contacts lubricated by oil-refrigerant mixtures using CFC-12 and various oils was studied by [4]. The researchers used counterformal contacts, area contacts and conformal contacts in their study. They concluded that the chlorine atom in CFC-12 serves to form protective surface films which effectively reduces friction and wear. Lubricant-refrigerant mixture using mineral oil and HCFC-22 was analyzed by [5]. Their results showed that the rate of change of pressure as seen by the lubricant-refrigerant mixture while circulation in the system was too fast to allow the mixture to reach equilibrium. The mixture concentration lagged behind the pressure-temperature changes in the system. Friction and wear characteristics in refrigerant atmosphere using CFC-12, mineral oil and synthetic oil were experimentally investigated by [6]. Their results showed that CFC-12 has Extreme Pressure properties. Chloride layer and fluorine were detected on the sliding surfaces in the post test analysis which contributed to the anti-wear properties. Their results also showed that the wear rates were reduced with increasing speeds or loads. An apparatus working on the principle of optical interferometry was developed [7] to study the film-forming capability in pressurized refrigerant atmosphere. One of their tests with CFC-12 and mineral oils showed that the refrigerant has a strong effect on reducing the oil film forming capability. This effect however decreased with a rise in oil temperature. Dry friction tests of a number of refrigerants including CFC-12 and HCFC-22 were performed by [8]. CFC-12 and HCFC-22 showed the highest seizure load amongst the tested refrigerants indicating the effect of Extreme Pressure. Although the tribological studies of refrigerants were not very large in number till the 1990s, but their results clearly showed that CFCs and HCFCs had good tribological properties especially for use in domestic, commercial and automobile applications. The viscosity of the lubricating oils decreased in refrigerant environment, which was unavoidable. However the formation of protective surface films made it possible for the compressor to run at very low lubricant viscosities and show good wear and friction characteristics.

Destructive effects of CFCs on the stratospheric ozone layer were published by [9] in 1974. This work clearly stated that chlorofluoromethanes can remain in the atmosphere from 40 to 150 years and lead to the destruction of the ozone layer by chemically reacting with it. Vienna Convention for the Protection of the Ozone Layer in 1985 was followed by the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987 [10]. Montreal Protocol was enforced in 1989 which banned the use of CFCs by the end of year 1995 in developed countries. HCFCs were suggested as transitional refrigerants. Their consumption was also limited by Montreal Protocol. Different countries adapted different phase out strategies of HCFCs. Having zero ozone depleting potential the focus shifted to hydrofluorocarbons (HFCs).

HFCs became the refrigerants of choice in the mid-1990s and they replaced CFCs and HCFCs in automobile, commercial and domestic refrigeration and air-conditioning systems. Various researchers worldwide started investigating HFCs with respect to their oil miscibility, their friction performance, their wear characteristics, etc. Some of the earlier studies focused on their direct comparison with CFCs and HCFCs. Amongst the HFCs, HFC-134a was suggested as the most suitable replacement for CFC-12. Studies on HFC-134a involving specific gravity, vapor pressure, vapor thermal conductivity, liquid viscosity and its overall physical and thermodynamic properties [11-13] made a direct comparison with CFC-12 and recommend it as the best replacement.

Mineral oils that showed good miscibility with CFCs and HCFCs, unfortunately were not compatible with HFCs. HFCs showed poor compatibility and miscibility in mineral oils. Synthetic oils with various additives were developed for HFCs. Using nine different polyalkylene glycols (PAG) with HFC-134a, wear tests were performed and compared to the performance of CFC-12/mineral oil by [14]. Their results indicated that the CFC-12/mineral oil showed no wear in a compressor connecting rod; however, all PAG/HFC-134a showed distress at the wrist pin. This study also concluded the oil/refrigerant miscibility to be the most dominant factor. Lubricant properties including solubility, thermal stability, viscosity, water adsorption, lubricant compatibility and lubricity of HFC-134a and synthetic oils were studied by [15]. Using 10 different synthetic oils with HFC-134a, the study [15] suggested esters, amides and polyalkylene glycols to be the most suitable oils for HFC-134a. The study [4] compared the friction and wear properties of HFC-134a with CFC-12 using different contact geometries. This study showed that CFC-12/oil mixture had much better wear results as compared to HFC-134a/oil mixtures. HFC-134a does not have any chlorine atom whereas the chlorine in CFC-12 forms protective surface films and decreases wear. The conclusion of the study [16] indicated that various kinds of additives were required for oils to be used with HFC-134a, whereas CFC-12 and HCFC-22 need no or very few additives. The experimental investigation [6] compared the tribological performance of HFC-134a and CFC-12 stated that the coefficient of friction and the fluctuations increase in HFC-134a environment, whereas the fluctuations and the friction coefficient decreases in the case of CFC-12. Friction experiments conducted under dry conditions [8] showed that the fluorine in HFC-134a had somewhat of a lubricating effect; however in comparison, CFC-12 and HCFC-22 showed better results. Similar studies [3, 17-20] compared HFCs with HCFCs. Almost all of the studies carried out to compare HFCs which CFCs and HCFCs concluded that that HFCs had poorer tribological properties in contrast to their predecessors. Due to the zero ozone depleting potential of HFCs, they are being used till date in a number of air-conditioning and refrigeration applications.

In 1997 Kyoto protocol to the United Nations Framework Convention on Climate Change [21] established binding limits on emissions of carbon dioxide and other greenhouse gases (GHG). The main source of the greenhouse emissions is the consumption of fossil fuel which produces carbon dioxide. Nitrous oxide, methane, perfluorocarbons (PFCs) and hydrofluorocarbons were identified as the other main contributors to global warming [22]. HFCs were recognized as major contributors to global warming and a phase out of HFCs has been planned for the coming years. A ban on non-confined direct evaporation systems using HFCs and PFCs was imposed in 2007. All F gases having 150 or more global warming potential will be banned as refrigerants in any hermetically sealed system from the year 2022. This directly affects HFC-134a, which has a global warming potential of 1430 for integrated time of 100 years [23].

These international regulations and bans have forced the refrigerant manufacturers and the air conditioning and refrigeration industry to find alternative refrigerants yet again. The challenge to come up with refrigerants which not only have the thermodynamic properties matching their predecessors but also having very low ozone depleting potential (ODP) and low global warming potential (GWP) is even greater.

The refrigerant industry has come up with potential future generation refrigerants having low OPD, low GWP and low flammability. Some of these refrigerants are already being charged in automotive and domestic air-conditioning and refrigeration systems. There has also been advice to shift towards natural refrigerants such as carbon dioxide and avoid the use of chemically formulated coolants which have proven to be harmful to the earth's atmosphere one way or another. The friction, wear and the overall tribological properties of these next generation refrigerants like Hydrofluoroolefins, Hydrofluoroether, and natural refrigerants like carbon dioxide are being studied by various researcher around the globe. This review paper focuses on the investigations carried out on the tribological performance of domestic, small scale commercial and automotive refrigerants.

2. REFRIGERANTS CONSIDERED

Ranging from chemically formulated to natural refrigerants, there are a variety of refrigerants available for use. The selection of a refrigerant depends on its application and place of use. Environmental legislations have banned the use of certain refrigerants over the years. This has forced the development of new refrigerants. Initially this paper presents the work done on CFCs and HCFCs in the 1980s and 1990s, which is followed by HFCs. After HFCs, natural refrigerants i.e. carbon dioxide and hydrocarbons are presented. At the end, recently developed refrigerants, Hydrofluoroolefins (HFOs) and Hydrofluoroethers (HFEs) are discussed.

Different researchers used different apparatus and varying geometries for the tribological analysis of refrigerants. This paper classifies the findings in terms of the refrigerant used in a study. Most of the studies are concerned with the investigation of an oil/refrigerant mixture, however some researchers have used a refrigerant only for their study. The reason for choosing oil/refrigerant mixture by most of the researchers is that in actual compressors the refrigerant gets mixed with the lubricating oil and the oil/refrigerant mixture then dictates the lubricating properties in a compressor. On the other hand some of the researchers say that if the true friction and wear properties of a refrigerant are to be investigated, then it should be tested independently from the lubricating oil.

Almost all of the studies have used the refrigerant in gaseous phase with the exception of a few investigators who used the refrigerants in liquid state in their study. Most refrigerants are in the gaseous phase under standard room temperature and pressure. The refrigerants are also mostly in gaseous phase when in a compressor is why most of the investigations are concerned with the refrigerant in vapor form. However the refrigerant does go under a phase change in a refrigeration cycle and turns from gas to liquid and then from liquid back to vapor. According to some researchers the true properties of a refrigerant as a lubricant can only be seen in liquid phase independent of a lubricating oil.

The published/reported studies are mainly concerned with simulating conditions present in a compressor. Some researchers have developed their own customized rigs for investigating the tribological behavior of refrigerants, some investigators have used actual compressors in their study, whereas standard tribo-testing machines have been utilized in the other studies. Many studies also include the influence of the materials under contact. Various different metals, metal alloys and hybrid contacts have been used in the earlier investigations. Recently the focus has shifted towards the investigation of surface coated contacts. The effect of surface texturing has also been investigated in the recent past. Table 1 summarizes all the refrigerants that have been discussed in this article along with their OPD, GWP and flammability.

Table 1. Refrigerants considered.

Refrigerant	ODP	GWP*	Flammability
CFC-12	1.00	10,900	Nonflammable
CFC-114	1.00	10,000	Nonflammable
HCFC-22	0.05	1,810	Nonflammable
HCFC-123	0.060	77	Nonflammable
HFC-134a	Zero	1,430	Nonflammable
HFC-32	Zero	675	Nonflammable
HFC-125	Zero	3,500	Nonflammable
HFC-407C	Zero	1,774	Nonflammable
HFC-404A	Zero	3,922	Nonflammable
HFC-245fa	Zero	1,030	Nonflammable
HFC-410A	Zero	2,088	Nonflammable
HC-600a	Zero	3	High
HC-290	Zero	3.3	High
HC-1270	Zero	0.01	High
R-744	Zero	1.00	Nonflammable
HFO-1234yf	Zero	4.00	Mild
HFO-1233zd	0.0002	1.00	Nonflammable
HFE-245mc	Zero	622	Nonflammable

**GWP values for 100 year based on the Fourth Assessment Report* [24].

3. CHLOROFLUOROCARBONS (CFCs)

The search for a nonflammable, colorless, tasteless, odorless and nontoxic refrigerant in the late 1920s led to the development of CFCs and HCFCs in 1928. CFCs are chemicals containing atoms of chlorine, carbon and fluorine. These nonflammable and nontoxic chemicals were used as solvents, blowing agents for packing materials and foam, in the manufacturing of aerosol sprays, and as refrigerants. Production of CFCs was banned by the end of 1995 in developed countries and from the year 2010 in developing countries by the Montreal Protocol.

Besides being nontoxic and nonflammable the thermodynamics qualities of CFC-12 made it an ideal candidate for automotive, domestic and small scale commercial air-conditioning and refrigeration systems.

A study based on the mixture of CFC-114 and CFC-12 with synthetic oil for screw compressors for heat pump applications was conducted by [2]. Small heat pumps are designed normally without oil separators, this is to allow relatively large amounts of oil to be entrained in the refrigerant circuit [2]. Figure 1 shows oil in a refrigeration system.

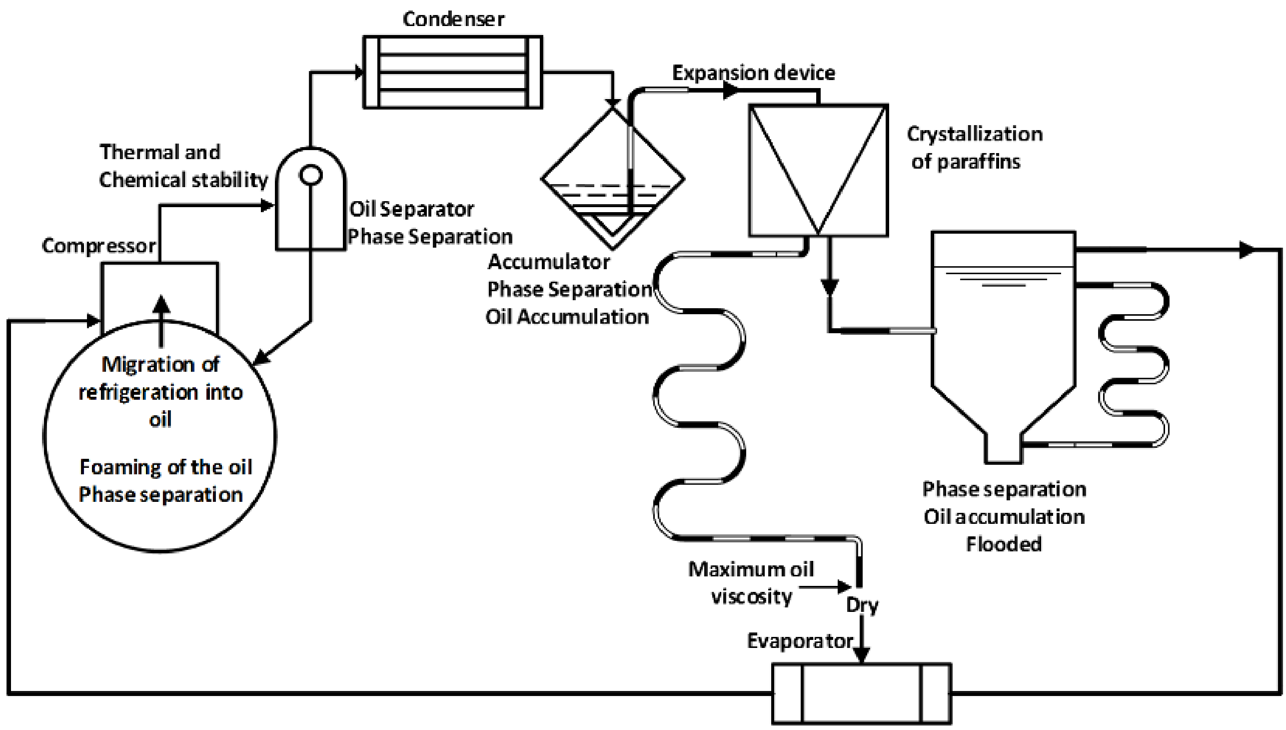


Fig. 1. Oil in a refrigerating system [2].

This [2] project was based on the study of the effects of the refrigerant on the oil density and oil viscosity. An oil having kinematic viscosity at 40 °C, 405 $mm^2\ s^{-1}$; density at 15 °C, 0.853 $g\ cm^{-3}$; flash point, 285 °C; pour point, −43 °C was used. The viscosities of pure CFC-12 with oil and pure CFC-114 with oil using pressure-proofed rolling ball viscometer were measured. The results showed a straight line relationship between the kinematic viscosity and temperature. CFC-114/oil mixture showed a lower viscosity compared to CFC-12/oil mixture. The viscosity of the oil/refrigerant mixtures decreases in both cases with increase in temperature, and also with increase in refrigerant concentration in oil. The viscosity of the lubricant has a direct impact on the lubricant film thickness which effects friction and wear. This study also compared their measured values with previously developed analytical equations and empirical relationships for calculating the viscosity and density.

A reciprocating semi-hermetic compressor, die cast aluminum connecting rod, cast iron piston, gray cast iron crank shaft, hardened steel wrist pin and steel-backed bronze main bearing was chosen for investigation by [14]. This study was done at five different conditions representing start/stop, high-compression ratio, normal load, high load and flooded start conditions. The purpose of the study was to evaluate the performance of CFC-12/mineral oil and its comparison to HFC-134a/synthetic oil. Nine different synthetic oils were used in this study with HFC-134a. All the synthetic oil combinations with HFC-134a showed wrist pin distress. CFC-12/mineral oil testing resulted in no connecting rod wear at the wrist pin probably due to the fact that CFCs form protective surface coatings on the interacting surfaces.

The tribological characteristics of the critical contacts in a rolling piston, in a swash plate and a reciprocating compressor have been studied by using a high pressure tribometer [4]. The critical contacts investigated in this study were the vane-piston contact in the rolling piston type compressor, the wrist pin bearing contact in the reciprocating piston type compressor and the shoe-plate contact in the swash plate type compressor. These three geometries represent counterformal, conformal and area contacts respectively. The vane-piston contact was simulated by a stationary hardened tool steel pin rubbing against an oscillating hardened cast iron plate. The wrist pin-bearing contact was simulated by a stationary case-hardened mild steel pin rubbing against an oscillating aluminum pad. Finally, the shoe-plate contact was simulated by a stationary circular bronze shoe rubbing against a rotating hardened ductile cast iron plate. This study used CFC-12/mineral oil and HFC-134a/synthetic oil mixtures. Their results of area contact showing the wear are presented in Fig. 2. CFC-12 chemically reacted with the bronze shoe producing $CuCl_2$ and very small amount of ZnF_2 as surface films. These films help lowering the wear by protecting the surface. Such phenomenon was not observed in the case of HFC-134a and it showed higher wear and friction. Similar wear results were observed for the counterformal and conformal contacts as CFC-12 produced $FeCl_2$ with iron. Friction is a complex phenomenon and occurs at the interface of two components in relative motion [25]. The results for the coefficient of friction for counterformal and conformal contacts of HFC-134a were found to be comparable to CFC-12.

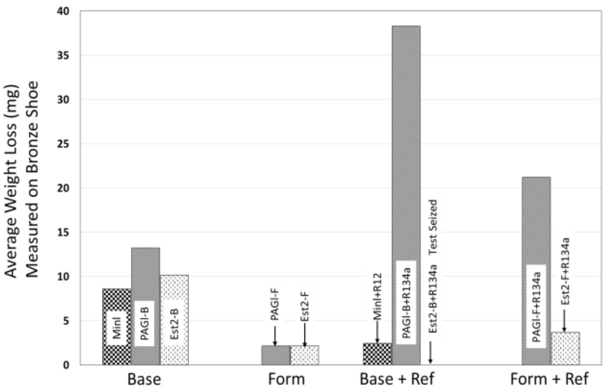


Fig. 2. Area contact wear results [4].

The miscibility of various synthetic oils was studied with HFC-134a and the lubricity of CFC-12 was compared to HFC-134a by [16]. It was concluded that oils used with CFC-12 require very few or no additives. Due to the fact that HFCs lack the ability to form protective surface films under normal compressor operating conditions, oils to be used with HFC-134a require various combinations of additives to improve performance.

A high pressure tribometer was used by [26] to experimentally investigate the wear and friction characteristics of the vane-piston contact of a rolling piston compressor. Cast iron piston running against M2 tool steel was the material pair studied. Different surface treatments for M2 steel were evaluated. Hardened steel samples were tested against gas, ion, and liquid nitrided, as well as boronized and TiN coated specimens. Using polyolester and alkylbenzene oils as lubricants, friction and wear were evaluated in HFC-134a, CFC-l2, argon, and air environments. The results of the study indicated that the diffusion processes, namely; liquid nitriding, ion nitriding, and boronizing did not offer any tribological benefits over hardened M2 steel under the conditions studied. Chemical vapor deposition (CVD) used to deposit TiN coatings lowered the wear magnitude than the other surface treatments because CVD process produces a smoother surface with more rounded asperities. The coefficient of friction and wear depth on the surface was higher with the TiN coated samples as compared with the other surface treatments. This was due to the sharp and very hard asperities formed by the CVD process. Figure 3 shows the results of the pin wear with respect to the testing environment. The results in Fig. 3 also show that the least amount of wear occurred in the case of refrigerant CFC-12 irrespective of the surface treatment.

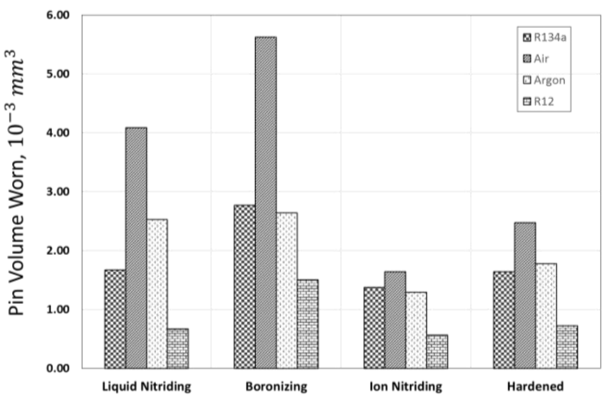


Fig. 3. Effect of test environment on pin wear [26].

Wear and friction characteristics in refrigerant environment with and without lubricants were investigated by [6]. A ring-on-disk apparatus was used in their experiments. The ring used was made of cast iron while the disk was made of leaded bronze. CFC-12 and HFC-134a along with nitrogen gas were investigated with and without synthetic lubricants. Figure 4 shows the comparison of wear rates and the friction coefficient obtained in this study.

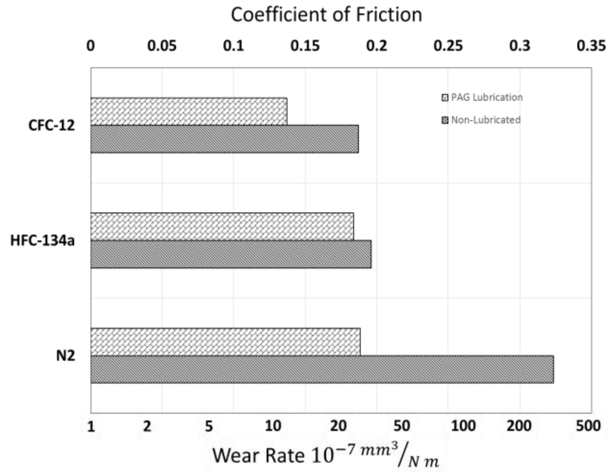


Fig. 4. Comparison of friction coefficients and wear rates in different gases with and without lubricant [6].

CFC-12 showed the lowest wear and the lowest coefficient of friction with and without the lubricant. In this study chlorine was detected on the bronze surface but not on the iron surface. Bronze also experienced more wear than the iron surface which suggested that exposure of an active fresh surface was necessary for the formation of a chloride layer. Another explanation could be that under the given conditions chlorine reacted more readily with the lead in bronze as compared to iron. The formation of a surface film gives CFC-12 Extreme Pressure properties. The difference between the wear of HFC-134a when tested with and without the lubricant is not as significant as compared to CFC-12 and nitrogen. Surface analysis of the samples tested under HFC-134a atmosphere without the lubricant revealed the presence of metal fluorides on the surface. This showed that HFC-134a also decomposed to form fluoride layers when used under more severe conditions, such as when running it without any lubricant.

A specialized optical interferometry equipment to investigate the film-forming capability of refrigeration lubricants was developed by [7]. Their results showed that CFC-12 had a better ability to form a film as compared to HFC-134a at elevated temperatures.

Roller steel bearings were used in a Shell Four Ball Test to study dry friction [8]. CFC-12, HCFC-22, HFC-32, HFC-125, HFC-134a, and nitrogen gas were used in this study without any lubricant. Seizure loads were studied, CFC-12 and HCFC-22 that contained chlorine molecules showed the highest seizure load, representing the effect of Extreme Pressure. The HFCs that did not contain chlorine showed the next heaviest seizure load. Surface analysis of the samples tested under HFCs revealed fluorine on the surface. This showed that the fluorine in HFC acted as an Extreme Pressure agent as well.

4. HYDROCHLOROFLUOROCARBONS (HCFCs)

HCFCs were used as refrigerants in freezers, refrigerators and air-conditioning systems. HCFCs structure resembles closely to CFCs, however HCFCs have lower ODP and lower GWP compared to CFCs. The use of HCFCs was allowed for a longer period of time due to their lower environmental impact compared to CFCs. HCFCs were also allowed as intermediate refrigerants while switching from CFCs to HFCs. However, the use of HCFCs in new equipment was banned in 2001 in UK. Amongst HCFCs, HCFC-22 was the most popular one. It was commonly used in process cooling, in automobile air conditioning systems, in small scale industrial units and in domestic refrigerators.

Tribological analysis in rolling piston type compressor using ferrous and nonferrous metals was conducted by [1]. Using HCFC-22, this study analyzed the lubrication conditions of journal bearings and the vane-tip using modified compressors. The results indicated that the scuffing behavior is sensitive to the refrigerant atmosphere. Scuffing is a complex phenomenon in which adhesive wear occurs under particular combinations of lubrication, contact pressure, friction and speed [27]. The scuffing load of the nonferrous metal bearings decreased with increase in refrigerant concentration. The contrary was observed for ferrous metals; with increase in refrigerant concentration the scuffing load increased for ferrous metal bearings. This may be due to the chemical reaction of chlorine with ferrous metals which results in the formation of chloride films on ferrous metals under these operating conditions. The increase in refrigerant concentration increased the chlorine in the system and resulted in the faster and thicker development of chloride films.

Optical interferometry was used [3] to study the effects of refrigerants on the lubrication of rolling bearing element used in screw compressors. Lubricant film thickness was evaluated with and without refrigerants. Mineral oil was used with HCFC-22 and synthetic oil was used with HFC-134a. The study concluded that the mechanism of lubrication of rolling element bearings operating in the presence of oil-refrigerant solutions is similar to that for oil only. The refrigerants reduced the lubricants viscosity as well as the lubricants pressure-viscosity coefficient. This study also used the equations presented by Hamrock and Dowson [28] to theoretically calculate the values of the central film thickness and compared them to their experimental results.

Lubrication of screw compressor bearings in the presence of HCFC-22 and HCF-134a was studied by [5]. Experiments were performed to determine the properties of some alternative compressor lubricants in bearing test machines. Tests included a ball bearing test, a taper roller bearing flange contact test and a test with sets of angular contact ball bearings. Different loads were used to study how the behavior of the refrigerant-lubricant mixture changes during the flow through a set of three bearings in each direction. The results showed that the compressors can be treated by elastohydrodynamic lubrication theory only when the refrigerant-lubricant is in equilibrium with the temperature and pressure at the bearing surfaces with fully-flooded conditions.

Tribological behavior using block-on-ring apparatus for polyolester base oil and formulated oils in HFCs and HCFCs refrigerant environment was evaluated by [17]. The ring was made of nickel chromium molybdenum steel and the block was made of tool steel. HFC-134a, HFC-407C, HFC-404A and HCFC-22 were used in this study. HCFC-22 gave the best performance due to the ability of HCFCs to form protective surface films on the interacting surfaces. Different additives were used in the lubricants with HFCs to match their performance to HCFC-22. Sulfur-phosphorus type additive together with aryl phosphate in HFC environment showed performance comparable to that of formulated alkylbenzene in HCFC-22.

Various HFCs and HCFC-22 were used by [18] to study; the hydrolytic stability, thermal stability, moisture removal effect, endurance of compressors and the endurance of refrigeration systems. This study concluded that alpha-branched acid rich polyester is most suitable for HCFC-22 and HFCs.

In the research done by [20] it was stated that because HFCs produce no Extreme Pressure effect in comparison to HCFCs, HFC-134a/oil mixtures require typically 50 % higher viscosity compared to HCFC-22/oil mixtures for the same wear rate. The conducted experiments investigated the possibility to increase oil concentration in the bearings for better lubrication. The conclusion of this study was to decrease flow rate of the oil-refrigerant mixture to get good bearing lubrication.

An interferometric Elastohydrodynamic (EHD) tester equipped with a pressurized vessel was used [29] to investigate the EHD film-forming characteristics of several oils with a number of refrigerants. The refrigerants used in this study were CFC-12, HCFC-22 and HFC-134a respectively. A ball-on-disk apparatus comprising of optical interferometry equipment to monitor and measure the oil film thickness was used in this study. Hamrock-Dawson's equations [28] were also used in this study to compare the experimental results with theoretical calculations. It was concluded that the EHD film thickness formed by oil/refrigerant mixture is the same as that of oil itself and increasing the amount of dissolved refrigerant in oil reduces not only the viscosity, but also the viscosity-pressure coefficient of oil.

A high pressure chamber capable of liquefying refrigerants was used by [30] to investigate the high pressure effects on HFC-245fa, HFC-134a and HCFC-123. The purpose of this study was to see the performance of these refrigerants as lubricants without using any oil. This was to look into the possibility of making compressors oil free. The refrigerants were liquefied and their share stresses were measured. Compared to HFC-134a and HCFC-123, HFC-245fa showed a smaller decrease in share strength with share rate. This study concluded that HFC-245fa has better mechanical properties and can be considered for bearing lubrication without any oil.

To study the compressibility of oil/refrigerant lubricants in elastohydrodynamic contacts a high pressure tribometer was used [31]. This study included mineral oils, synthetic oils, HCFC-22 and HFC-134a. The study concluded that stiffness of the lubricating oils increases more with HFC-134a as compared to HCFC-22.

A bearing test rig was designed and equipped with a capacitance measuring device to study the bearing on-line lubrication status [32]. HCFC-22 and HFC-134a were used as refrigerants along with lubricating oils. The metal to metal contacts were counted and the microscope analysis of the samples was done post testing. The study showed that there were more metal to metal contacts in the case of HFC-134a as compared to HCFC-22. The chlorine in HCFC-22 showed Extreme Pressure effects in comparison to HFC-134a which did not produce any Extreme Pressure effects and does not have chlorine in its molecular structure. Resultantly HFC-134a showed more wear in contrast to HCFC-22.

A modeling and experimental assessment of HCFC-123 for lubricating rolling elastohydrodynamic (EHD) circular contacts was performed by [33]. Their results revealed that refrigerants indeed can build up a satisfactory film thickness for lubricating EHD rolling point contacts. Their study used full numerical models developed by [34-36], analytical elastohydrodynamic film-thickness expressions developed by [37, 38] and experimental work. Their experiments were performed using a ball-on-disk tribometer equipped with an interferometry facility to measure the film thickness under pure rolling conditions.

5. HYDROFLUOROCARBONS (HFCs)

HFCs are synthetically produced refrigerants containing hydrogen, fluorine and carbon. HFCs were introduced after the Montreal Protocol. The Montreal Protocol which focused primarily on the reasons for the depletion of the ozone layer put restrictions and bans on the production and use of CFCs and HCFCs. HFCs had thermodynamic properties matching their predecessors [11-13, 39, 40], which resulted in their extensive use as replacement refrigerants. HFCs started being widely used as coolants instead. Since the early 1990s, HFCs have been widely used in a number of different fields and applications. The global warming implications of HFCs were not considered at the time of their introduction, however the high global warming impact of HFCs was realized later. Kyoto Protocol addressed the damaged being done to the global atmosphere and the responsible attributes and chemicals causing global warming. A restriction was put on HFCs and HFCs are now in the process of being phased out. The phase out of HFCs started in 2015 in Europe. By the end of 2030 it is expected that HFC availability will be cut by 79 % in Europe.

HFCs remain the most investigated refrigerants from the tribological view point. This is because of their unique position in history. HFCs were initially compared to their predecessors to see how they performed compared to CFCs and HCFCs. A number of studies showed that HCFCs and CFCs have better tribological performance as compared to HFCs especially while being operated in a compressor atmosphere. Various additives and different blends of synthetic oils were developed and investigated to improve the performance of HFCs over the years. CFCs and HCFCs were used as a benchmark to analyze HFCs. After being introduced in the market on a commercial scale, further studies were still conducted on HFCs to look at their behavior under various different operating conditions. Now a days the potential successors of HFCs are being compared with HFCs to evaluate their performance. Most of the new studies involve the use of future generation refrigerants and HFCs. This helps making a comparison between the various refrigerants under identical operating/testing conditions.

Amongst the HFC refrigerants, 1,1, 1,2-tetrafluoroethane (HFC-134a) has been the most tested and investigated refrigerant from the view point of tribology. This is because HFC-134a was deployed for systems that previously used CFCs and HCFCs. A number of studies involving HFCs are discussed below. HFCs are also discussed alongside CFCs, HCFCs, natural and future generation refrigerants.

A pin-on-disk and a ball-on-disk configuration was used [41] in a test rig designed to simulate the conditions of a compressor. The purpose of this investigation was to study various refrigerant oils under HFC-134a environment and compare them to CFC-12. Mineral oils, alkylbenzenes, and polyalpha olefins tested immiscible with HFC-134a. However ester oils and PAG were miscible with HFC-134a. This study suggested that ester oils are preferable at start and stop conditions. PAG demonstrated good lubricity in extreme pressure conditions and HFC-134a/PAG mixture showed friction coefficient similar to CFC-12/mineral oil. PAG increased friction considerably under boundary lubrication, however CFC-12/mineral oil and HFC-134a/ester oil indicated good lubricity in that condition. Easter oil/HFC-134a showed highly unstable friction behavior due to the lack of extreme pressure durability. PAG on the other hand has extreme pressure enhancement and produced a stable lubricating film by the chemical reaction of metal surfaces in the presence of HFC-134a environment.

Bearing steel ball and bearing steel plate were used by [42] in a reciprocating test rig to investigate the friction and wear characteristics of polyalkylene glycol (PAG) and a polyol ester (POE) oils. The behaviors of these oils along with the effect of additives were examined in HFC-134a environment. Additives improved the friction and wear performance in both the lubricants. PAG showed good wear and friction characteristics in HFC-134a environment by forming fluoride on the rubbing surfaces. POE displayed poorer friction and wear characteristics above a transit temperature because an adsorbed POE film prevented the formation of fluoride. However POE produced very good tribological performance at temperatures below the transient temperature. TCP significantly improved the tribological performance of PAG due to the adsorption film of TCP in low temperature range and formation of phosphate in high temperature range. TCP did not improve the friction and wear characteristics of POE because POE prevented the adsorption of TCP on the rubbing surfaces. MoDTC with POE in HFC-134a environment lowered the friction coefficient by forming MoS_2 in spite of no oxygen in the environment below the transient temperature. Friction characteristics of PAG were not improved with the addition of MoDTC as no MoS_2 was formed with PAG in HFC-134a environment.

A sealed block-on-ring wear tester was used [43] to experimentally investigate the tribological characteristics of various lubricating oils under HFC-134a environment. The lubricants used were linear polyolesters (L-POE), branched polyolesters (HS-POE), polyvinylethers (PVE) and polyalkylene glycols (PAG). PAG and PVE displayed better anti-wear performance compared to linear and branched POE under boundary lubrication conditions. POE produced carboxylic compounds under boundary lubrication. These compounds were produced by POE's reaction with iron. These reactions occur due to the $C = O$ bond present in POE. These compounds are easily removed by rubbing from the friction surface. PVE and PAG have no $C = O$ bonds which explains why POE showed significant wear in comparison to PVE and PAG. PVE has higher resistance to breakdown under shear stress and has the ability to form a thick oil film in elastohydrodynamic lubrication region, this protects the rubbing surfaces from scuffing and wear.

A domestic compressor test-rig was manufactured by [44] to study the wear behavior of piston/gudgeon pin by using HFC-134a in hermetic compressors. Different synthetic lubricants were used with HFC-134a in this study. The results showed that higher viscosity lubricants produced minimum plastic deformation. Higher the viscosity higher is the film thickness resulting in lesser asperity interactions resulting in lower wear.

Refrigerant/lubricant mixtures were tested against: aluminum alloys, surface treated 356 aluminum alloy and an aluminum composite [45, 46]. Pin-on-disk line contact geometry was used in this study in which the pin was composed of carburized steel and the disk was of aluminum based materials. The study was divided in two parts. The first part consisted of aluminum/steel contacts lubricated by HFC-134a/polyester oil and HFC-134a/polyalkylene glycol oil mixtures. Amongst the aluminum alloys tested, 390-T6 die cast alloy showed the best wear resistance because it had the highest hardness. Due to the fact that SiC particle reinforcement provide very good wear resistance, the amount of wear decreased with increasing silicon content in aluminum alloys [47]. The wear resistance was not improved by conventional anodizing techniques of the 356 aluminum alloy because the hard layers cracked under high contact stress causing an increase in wear. Good wear resistance was observed in hard anodizing of 356, however it increased the wear on the counter face. In comparison to the PAG/HFC-134a mixtures, Ester/HFC-134a mixtures provided better protection of the aluminum alloys due to the ability of the esters to form bidentate bonds with aluminum. Increased amount of HFC-134a showed extensive surface fatigue on 356 aluminum. In the second part of the study, 390-T61 and 356-T61 aluminum alloys were tested in various refrigerant/lubricant mixtures. HFC-134a, HFC-407C, HFC-410A and HCFC-22 refrigerants were used with different lubricants. No significant difference in lubricity of alkylbenzene and mineral lubricants when used with HCFC-22, HFC-407C and HFC-410A was observed. This study also showed that at sufficiently high partial pressures, HFCs chemically react with the freshly exposed aluminum and increase the brittleness of aluminum alloys.

A pin-on-disk setup was used [48] to study the lubricity of HFC refrigerant oils in a scroll compressor. This study involved the use of HCFC-22, HFC-407C, mineral oil and polyvinylether (PVE) oil. Two types of aluminum alloys against cast iron were used in this study. The results showed that there was a noticeable difference in the wear amounts of HCFC-22/mineral oil and HFC-407C/PVE. The effect on wear of increasing the silicon content in the aluminum alloys showed that it was possible for HFC-407C/PVE to have wear as low as HCFC-22/mineral oil. Silicon content largely influences the anti-wear performance by suppressing wear in aluminum alloys.

Table 2. Properties of various coatings and vane material [49].

Vane	Hardness (Hv)	Deposition method
Original	950	-
TiN(I)	1900	Arc ion plating
TiN(II)	1600–1800	RF magnetron sputtering
TiAIN	2700	Arc ion plating
WC/C	1000	Magnetron sputtering
DLC	2000	Dual ion beam sputtering
Carbon vane	458	-
Ion nitriding	1150	Pulse plasma nitriding

A vane-on-disk setup comprising of Ni–Cr–Mo gray cast iron disks and vanes comprising of various coatings and materials was used [49] to study the tribological characteristics of HFC refrigerants in rotary compressors. Table 2 shows the various coatings and vane materials used in this study. The surface roughness and the coating thickness values have not been mentioned in this table, these values can be seen in the original table given in [49]. Tests were conducted using HFC-407C refrigerant with and without POE oil. One the results for wear obtained without using lubricant and by using the refrigerant only is shown in Fig. 5.

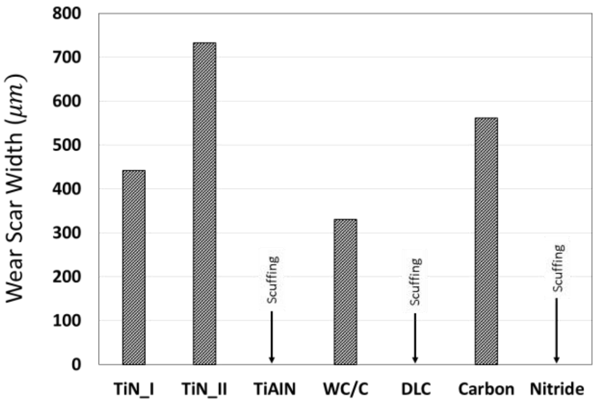


Fig.5. Wear scar width in HFC-407C only, tested in normal load of 440 N, speed of 70 rpm, 20 °C and test duration of 1 h [49].

Based on the results obtained in this study, the conclusions were that TiAlN (titanium aluminium nitride) and DLC (diamond-like carbon) are very hard coatings and are not suitable, because they produced high friction and severe wear on the roller. Good wear resistance was shown by TiN coated vane. Ion plating showed lesser wear compared to magnetron sputtering. Ion nitriding proved unsuitable as it was not good enough to sustain the cyclic stress. WC/C (tungsten carbon carbide) coating showed the best tribological performance which was probably due to the formation of a durable tribo-film on the mating surfaces.

Three different types of ester oils were used by [50] with HFC-134a to study the impact of lubricant viscosity on the wear of hermetic compressor components. Tribological behavior of the conforming contact between hardened steel gudgeon pin and die-cast aluminum alloy connecting rod of a reciprocating compressor were investigated. The conclusion was that the lubricant viscosity plays a major role in governing the tribological properties of the system. Low viscosity lubricants resulted in boundary lubrication regime which produced high friction, severe wear and material transfer. Increase in the lubricants viscosity shifted the system towards the mixed lubrication regime which improved the wear and friction of the system.

A shoe-on-disc geometry to simulate the plate/shoe contacts in a swashplate automotive air conditioning compressor was used in an experimental study conducted by [51]. Starved lubrication conditions were used to study the scuffing characteristics of 52100 steel against 390-T6 aluminum–silicon alloy. All tests were conducted with HFC-134a and PAG lubricant in a high-pressure tribometer. Four different shoe geometries were used to study the effects of sliding velocity, degree of lubrication starvation, contact geometry, skewness, surface roughness and the effect of a tin coating on scuffing. Crowning is used to help the shoe/plate contact generate hydrodynamic films, a perfectly flat and smooth shoe supported at its geometrical center theoretically is unable to generate these films. The groove or dimple helps trap lubricant and debris during operation. However the groove or dimple can be detrimental under starved lubrication conditions. In starved lubrication conditions the lubricant supplied is not sufficient for a groove or dimple to act as an effective reservoir. Scuffing results of 390-T6 AI on the crowned shoe, crowned shoe with dimple and crowned shoe with groove are shown is Fig. 6. The geometries with a dimple or groove in the crowned shoe resulted in higher peek pressures and temperatures.

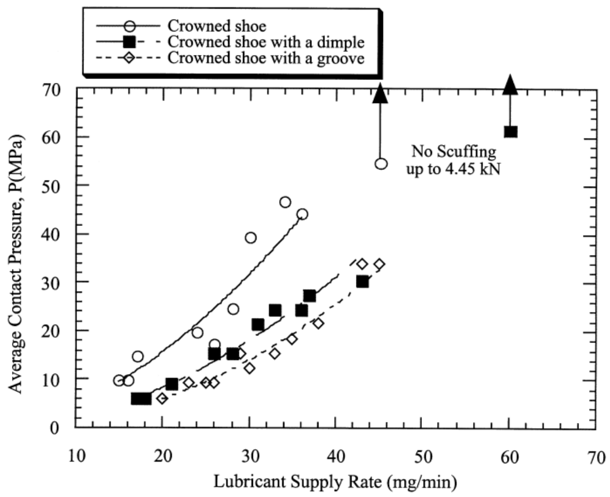
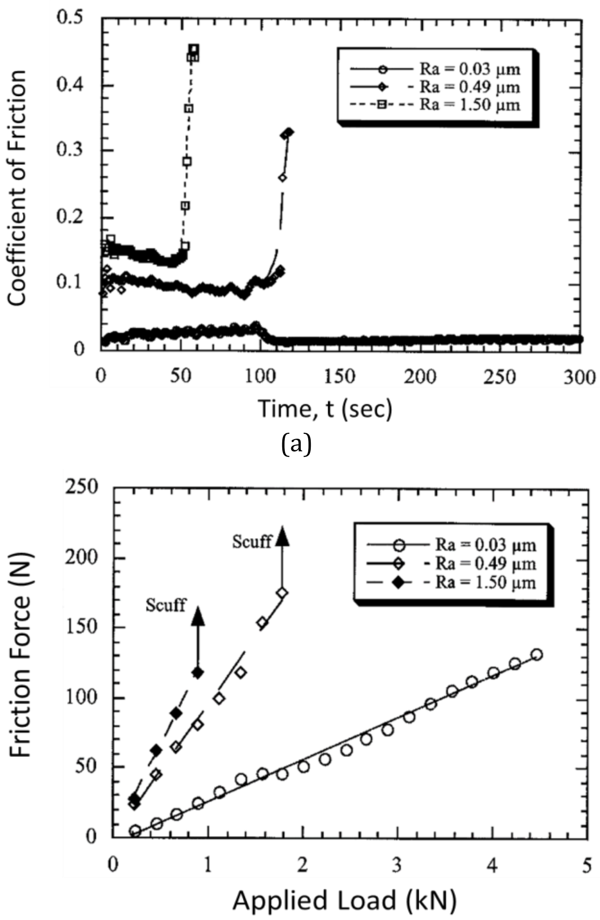


Fig. 6. Scuffing results for 390-T6 Al obtained with various crowned shoes. Sliding velocity: 1.86 $^{m}/_{s}$ [51].

The influence of surface roughness on scuffing was studied using 390-T6 aluminum discs with three different values of surface roughness against crowned shoes. The results of the effects of change in surface roughness on the coefficient of friction and friction force are shown in figures 7 (a) and 7 (b) respectively.



(a)

(b)

Fig. 7. Variation of coefficient of friction and friction force for different surface roughness. Lubricant supply rate: 40 $^{mg}/_{min}$; sliding velocity: 1.86 $^{m}/_{s}$. (a) Coefficient of friction, (b) Friction force [51].

Improved surface finish having lower surface roughness gave a lower value of the coefficient of friction and the friction force. The results of the scuffing resistance with change in the lubricant supply rate at various sliding velocities showed that for a given lubricant supply rate, the scuffing pressure decreases with increase in the sliding velocity, higher sliding velocities result in higher lubricant entrainment and an increase in the lubricant film thickness. No apparent effect was observed by changing the skewness in this study. The effect of tin coatings showed that coated discs offer better scuffing resistance than the uncoated discs. This is due to the low shear strength characteristics of tin. The conformity of the sliding surfaces is increased by tin, because tin deforms quickly and results in lower local temperatures and pressures. Tin coating acted as a temporary lubricant and also aided initial running-in by covering surface irregularities.

Using a ball-on-disk apparatus the lubrication of rolling element bearing with HFC was studied by [52]. Viscosity, pressure–viscosity, and the film thickness data for three polyolester oils was studied and it was concluded that branched lubricants give the benefit of a higher pressure–viscosity coefficient under normal conditions. However a branched lubricant is more susceptible to dilution by the refrigerant compared to a linear lubricant. To obtain maximum effectiveness, the lubricant should be formulated with as little branched acids as possible.

The solubility, viscosity and oil film thickness of HFC-134a, HFC-125 and HCFC-22 were studied with POE by using a ball-on-disk apparatus [53]. Increase in gas pressure increased the solubility of the refrigerant in the lubricant. HCFC-22 showed the highest solubility and HFC-125 revealed to be the least soluble refrigerant in POE. This resulted in HFC-125 having the highest film thickness and HCFC-22 having the least film thickness. The results of the influence of the gas pressure on the film thickness showed that the oil film thickness decreases with increasing gas pressure. The solubility of the refrigerants in the lubricating oil increases with increasing gas pressure, the increased solubility of refrigerants decreases the lubricants viscosity which results in lowering of the film thickness. HCFC-22 displayed the highest decrease in the oil film thickness and HFC-125 displayed the least decrease in the oil film thickness by increasing the gas pressure. The film thickness increased with increasing rolling speed due to higher lubricant entrainment.

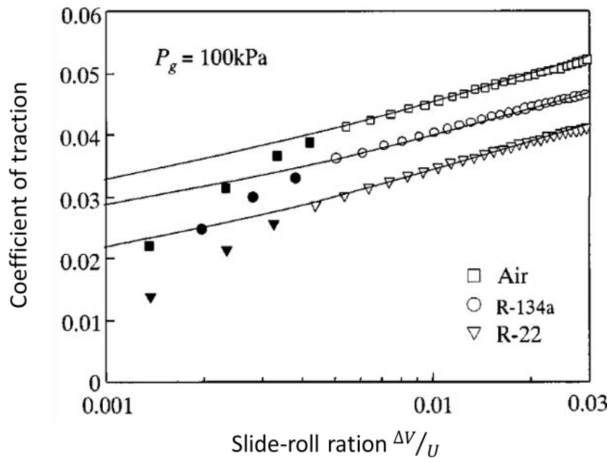
Experimental investigation using hermetically sealed refrigerating compressors to compare the tribological performance of PVE lubricants to POE lubricants using HFC-134a was done by [54]. Their investigation included the study of the conformal contacts between the small end of the connecting rod and the gudgeon pin as well as observing the compressor vane plates and the large end of the connecting rod. No clear difference was seen in the tribological performance of PVE and POE lubricants under the tested conditions.

A number of fluorinated alkyl aryl ethers were evaluated by [55] as refrigerant lubricants with HFC-134a. The fluorinated alkyl aryl ethers showed high miscibility with HFC-134a along with high stability, very good lubricity, and low moisture absorption.

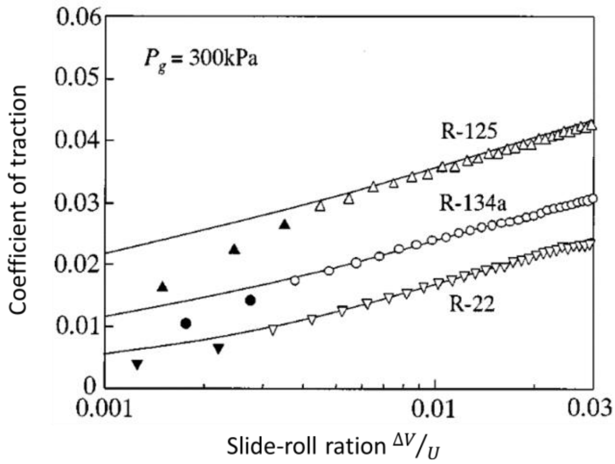
A case study to evaluate the overall influence of HFCs compared to CFCs on the environment was done by [56]. Factors like the contribution of the individual compressor components to human toxicity, the contribution of the individual compressor components to acidification, the electricity consumption to make the individual components of a compressor, etc. were discussed in this study. A comparison on the overall effects of CFC compressors was made to the overall environmental effects of HFC compressors. Although CFCs are labelled as being more harmful to the atmosphere [57], it was indicated by this study that CFC systems would have a lower impact on the environment as compared to HFC systems keeping in view the complete life cycle of each individual component of a compressor from material extraction, to fabrication to disposal.

A reciprocating ball-on-disk apparatus was used [58] to investigate the effects of HFC-134a on the solubility, viscosity and lubricant film thickness with PAG, POE and PVE oils. The study concluded that the dissolving of HFC-134a in the lubricants is an exothermic reaction. The dissolution of HFC-134a in the lubricants worsened the wear characteristics of lubricants by reducing their viscosity. The mean molecular weights of the lubricants also effected the viscosity. There was a decrease in viscosity reduction with an increase in the ratio of the HFC-134a solubility to the mean molecular weight of the lubricant.

HFC-125, HFC-134a and HCFC-22 were used with POE lubricant by [59] to study the rheological properties of polyolester oil under elastohydrodynamic (EHD) contact conditions in refrigerant environments. Analytical work as well as experimentation involving a ball-on-disk EHD tester were used in this study. The results of the coefficient of traction of the refrigerants at two different gas pressures with respect to the slide roll ratio are shown in Figs. 8(a) and 8(b) respectively. HFC-125 showed the highest coefficient of traction and HCFC-22 showed the lowest coefficient of traction. The values of the coefficient of traction decreased with an increase in the gas pressure. The effect on the effective viscosity-pressure coefficient and the effect on the representative stress with change in the gas pressure of all three refrigerants showed that, the values of the effective viscosity-pressure coefficient decreases while the value of the representative stress increases with increasing gas pressure. The results of the viscous volume with the molecular volume of the mixture are shown in Fig. 9. The results shown in Fig. 9 indicated that the relation of the viscous volume with the molecular volume can be represented by a single line irrespective of the refrigerants.



(a)



(b)

Fig. 8. Traction curves in some refrigeration environment. Solid lines are the calculated results based on the work described in [60] and the symbols are the measure data (a) at gas pressure of 100 kPa, (b) at gas pressure of 300 kPa [59].

It was also concluded by [59] that the POE characteristics in refrigerant gases are governed primarily by the pressure-viscosity coefficient.

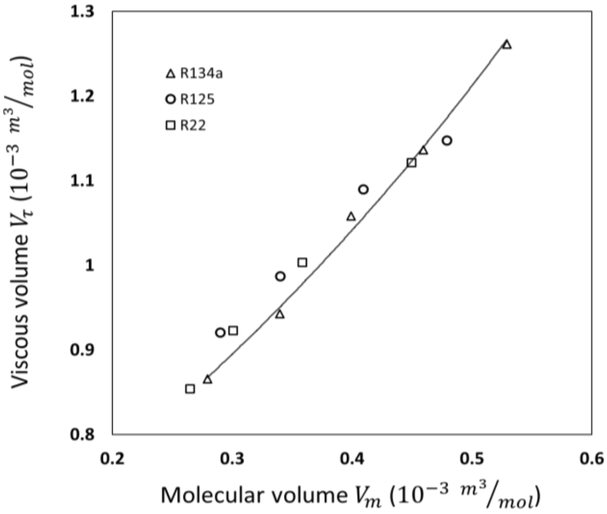


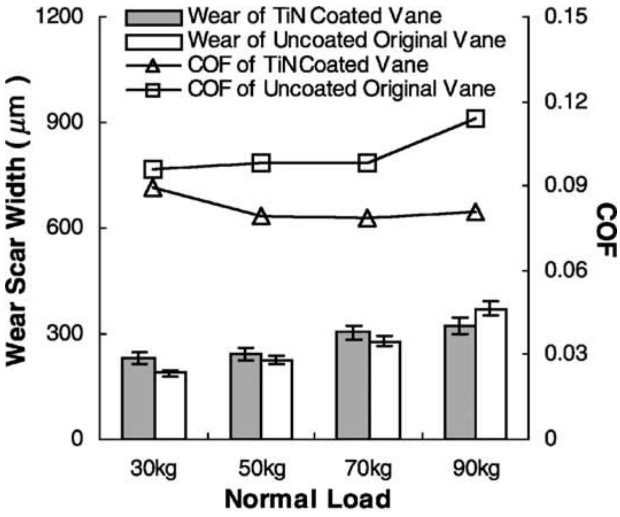
Fig. 9 Viscous volume versus molecular volume of refrigerant/POE mixture [59].

The elastohydrodynamic lubrication film in the presence of HFC-134a and POE lubricant was studied by [61]. This work involved the use of a ball-on-disk apparatus along with the use of analytical equations developed by [62] and [63]. The results of this study showed that a decrease in refrigerant concentration at the inlet region increased the elastohydrodynamic lubrication film thickness, decrease in refrigerant concentration increases the oil's viscosity increasing the film thickness. The concentration distribution of HFC-134a got affected by the oil temperature, the sliding velocity and the refrigerant concentration in the lubricant.

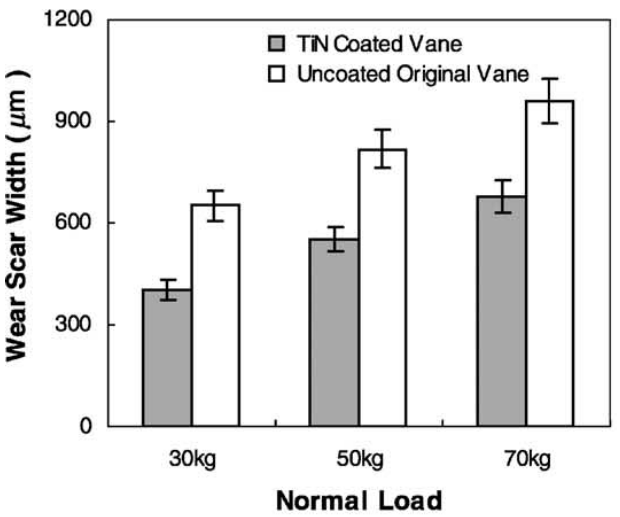
A pin-on-disk high pressure tribometer consisting of Al390-T6 discs and 52100 steel pins was used to investigate the effects of surface roughness of engineering surfaces by using HFC-410A and POE oil [64]. Factors like core fluid retention index, bearing area ratio, bearing ratio, surface roughness, skewness and kurtosis were studied. Highly negative skewness was observed in the mildly-worn surfaces supporting the theory that mildly worn asperities result in a more negatively skewed surface by revealing lesser peaks than valleys and pits. Change in kurtosis did not give any significant results. This study also concluded that the functional parameters or indices derived from bearing area curve, namely the fluid retention index and the surface bearing index can be used to draw sound conclusions of the tribological progression of roughness. The functional indices remained almost constant on the virgin surfaces, but with the surface approaching scuffing, the effects of progressive wear related to increased bearing index and a decreased fluid retention capability were observed.

In continuation of their [56] previous case study, an experimental test rig was built to monitor slight variations in the electrical power consumption by a reciprocating hermetic compressor [65]. The purpose of this investigation was to study the environmental impacts of a domestic refrigerator. The tribological characteristics of the aluminum alloy connecting rod and the steel gudgeon pin were also studied using CFC-12/mineral oil and HFC-134a/different synthetic lubricants. Furthermore, a comprehensive life cycle assessment on a domestic refrigerator was done to help quantify the environmental burdens. The experimental results showed that overall there was more damage to the parts in HFC-134a environment than that obtained from the CFC-12 tests. The electrical energy consumption when using CFC-12 was thus found to be substantially less as compared to HFC-134a. A four-ball test was done on oil samples before and after being tested in the compressor, the Extreme Pressure performance of a synthetic lubricant was observed to deteriorate more than that of mineral oil. Based on these results, this study concluded that HFC-134a based domestic refrigerators will contribute more towards the environmental damage as compared to CFC-12 based domestic refrigerators.

HFC-410A was used with POE lubricant to study the friction and wear of rotary compressor vane-roller surfaces using a vane-on-disk setup [66]. The disk was made of Ni–Co–Mo gray cast iron and a TiN coating using physical vapor deposition technique was applied to the vane made of high speed tool steel. Tests were conducted at different normal loads and speeds. A few of the results obtained in this study are shown in Fig. 10. TiN coatings improve the tribological characteristics of sliding surfaces which resulted in the better performance of the TiN coated samples as compared to the uncoated ones. The coefficient of friction as well as the wear on TiN coated samples was less as compared to the uncoated samples. The difference in the performance of the coated and the uncoated samples became more apparent with an increase in normal load and an increase in RPM. Effect of surface roughness was also studied by including TiN coatings of three different surface roughness in this investigation. The results of the effect of the surface roughness are shown in Fig. 11. Based on these results it was concluded that there exists an optimum initial surface roughness value which improves the load carrying ability and prolongs the wear life of interacting surfaces.



(a) 100 rpm



(b) 500 rpm

Fig. 10. Wear scar width of the vane tip under various normal loads and sliding speeds [66].

Employing ten different polymers as potential bearing materials, six blended polymers and four unfilled polymers; a high pressure pin-on-disk tribometer was used to examine the tribological performance of polymer/metal contacts under HFC-134a environment [67]. The disks were made of cast iron and aluminum alloys and pins were made of the various polymers. It was concluded that overall all the blended polymers have superior tribological properties compared to unfilled polymers and metals.

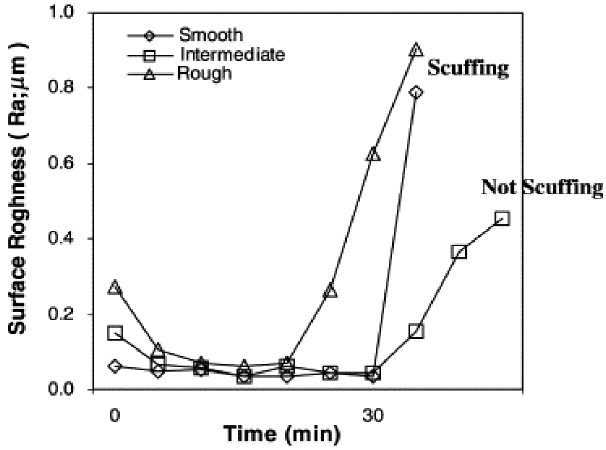


Fig. 11. Changes of surface roughness depending on the initial surface roughness [66].

A pin-on-disk apparatus comprising of gray cast iron disks and pins made of composites of different blends of polytetrafluoroethylene (PTFE) with aromatic thermosetting polyester (ATSP) under HFC-134a refrigerant were investigated by [68]. Controlled tribological experiments simulating an air conditioning compressor environment using ATSP/PTFE compositions, as well as four dissimilar commercially available composites containing graphite, carbon fibers, and PTFE were used. It was found that the newly synthesized composites showed very good tribological properties having very low friction and wear. ATSP did not significantly change the friction coefficient while it was shown that greater amounts of ATSP used in the blend lead to lower wear. However, lower friction coefficient values were obtained with increasing amounts of PTFE due to material transfer and development of a transfer film on the disk surface.

A shoe-on-disk setup in a high pressure tribometer was used [69] to investigate the tribological behavior of PEEK, PTFE and Fluorocarbon based polymeric coatings in HFC-134a environment for use in air-conditioning and refrigeration compressors. The shoe and pin were made of 52100 steel while the disk was made of cast iron and coated with different polymeric coatings. The experimental results indicated that in comparison to the other polymeric coatings, PEEK/PTFE coating performed slightly better in terms of wear and friction. In spite of the aggressive tribological conditions, the transfer of films from the disk coating to the 52100 steel shoes enabled the interface to operate without overheating.

Another study involving the tribological investigation of four different polymer based coatings for air-conditioning and refrigeration compressors was done [70]. A high pressure pin-on-disk tribometer with HFC-134a was used. It was found that compared to other coatings, in terms of the tribological performance, PEEK/PTFE coating performed better. This enhanced performance is associated with the arrangement of polymers in PEEK/PTFE coatings. PEEK is positioned below which provides wear resistance and strength and is responsible for the good adhesion with cast iron. PTFE particles migrate to the top (surface) and are responsible for supplying C_iF_j species to the wear track which contributes to lowering the friction.

Compressor performance in HFC-32 atmosphere was studied by [71]. HFC-32 has zero ozone depleting potential and has a GWP value of only about $1/3$ of HFC-410A. A comparison of HFC-32 with HFC-410A using PVE and POE lubricants was done to evaluate the reliability, durability and lubricity of a compressor in these refrigerant atmospheres. The reliability and durability of the compressor was studied by performing drop-in tests using an actual composer and the lubricity was tested using a hermetic block-on-ring test machine. The study revealed that HFC-32 has poor miscibility with conventional oils that are normally used with HFC refrigerants, the viscosity dropped more in case of using HFC-32, HFC-32 decomposed easily and generated organic acids that caused corrosion. New-PVE and New-POE have to be used with HFC-32 instead. Overall HFC-32 refrigerant was difficult to handle, it showed poor stability and generated acids that caused corrosion and abnormal wear of sliding compressor parts.

The tribological performance of PEEK and PTFE-based polymeric coatings with HFC-134a was also done by using a pin-on-disk setup [72]. Both the pin and the disk were made of gray cast iron with the disks being coated with various polymeric coatings. Scuffing experiments and the effect of transfer films was studied. The coatings showed worse performance in the presence of liquid lubricants than under dry conditions. This was because the formation of transfer films was prevented by lubricants. Under fretting conditions, the tribological performance of polymer coatings was highly influenced by the ability of the polymers to form transfer films on the metal counter face.

A study to investigate the effects of surface roughness on polymer films under unlubricated conditions using a pin-on-disk setup and HFC-134a as refrigerant was done by [73]. Pins made of various polymers were tested under unlubricated unidirectional conditions against gray cast iron disks. Polymer pins having high surface roughness produced discontinuous transfer layers while pins with low surface roughness produced a continuous transfer layer of polymer on the surface of the cast iron.

A new high pressure viscometer that can operate with oil/refrigerant mixtures at elastohydrodynamic lubrication was designed and fabricated by [74]. Various concentrations of HFC-134a were measured with POE oils using this high pressure viscometer.

A block-on-ring tribometer was used [75] to study the tribological characteristics of POE refrigeration oils under HFC-410A and HFC-32 refrigerants. The study concluded that lubricating film formation is affected by both the refrigerants and the base oils. It was found that the TCP in POE lubricant formed a lubricating film on the sliding surfaces under HFC-410A which enhanced the tribological performance. HFC-32 however, interfered with the formation of phosphate films. The high reactivity and polarity of HFC-32 with nascent metal surfaces prevented TCP from adsorbing to the iron on the sliding surfaces.

6. NATURAL REFRIGERANTS

Water, air, carbon dioxide, ammonia and hydrocarbons are considered to be the most environmental friendly and natural occurring refrigerants. Ammonia has been used for a long period of time in large industrial systems as a refrigerant and is still being used in large industrial applications. Water and air have been used as coolants in engineering and domestic applications since ancient times. Air and water are still being used in various applications for cooling purposes, but are not used as refrigerants due to their thermodynamic limitations. Carbon dioxide is also a good refrigerant which sublimes under normal atmospheric temperature and pressure. It has been used for cooling purposes but its utilization in refrigerator compressors is still under investigation. Hydrocarbons are found in crude oil and possess good thermodynamic qualities. Hydrocarbons are being used in commercial, domestic and industrial refrigerators, fridges and heat pumps. Their flammability is however a big concern. Hydrocarbons and carbon dioxide are discussed from a tribological view point in sections 6.1 and 6.2 respectively.

6.1 Hydrocarbons (HCs)

Hydrocarbon refrigerants are nontoxic, natural refrigerants that have zero ozone depleting potential and minimal global warming potential. Hydrocarbons which are extracted from crude oil are environmentally safe and efficient refrigerants. Hydrocarbon refrigerants are considered up to 50 % more efficient thermal conductors than fluorocarbon refrigerants. Hydrocarbons also have lower operating pressures than fluorocarbon refrigerants which results in lower power consumption and cost savings. Many European manufacturers of domestic and commercial refrigeration equipment are using hydrocarbon refrigerants in their compressors. Amongst hydrocarbon refrigerants Isobutane (HC-600a) is found in most domestic freezers and fridges while Propane (HC-290) is used mostly in commercial refrigeration and heat pump applications. The greatest challenge in handling and designing a cooling system based on hydrocarbons is their extremely high flammability. This is why they have not been used as frequently as HFCs and also have not been deployed in automotive air-conditioning systems. This section covers the tribological investigations done by various researchers on hydrocarbons.

A study involving the use of a modified micro-friction pressurized test rig with a pin-on-flat configuration was conducted by [76]. HC-600a and HFC-134a were used as refrigerants with synthetic and minerals oils. Friction and wear tests were performed on aluminum and steel samples. Mineral and synthetic oils with and without various additives were tested using HFC-134a/POE as benchmark. The results showed that the additised mineral oils had very low wear rate and formed a good boundary film. High levels of carbon were found at the pin contact with mineral oil indicating that any boundary layer developed by using mineral oil is more durable than that developed by using POE lubricant. In case of additised POE, deposition was present at the plate but not at the pin. The wear rate was higher in the beginning, which reduced as the contact geometries became more favorable. Initially the contact stresses are high resulting in the removal of any films by abrasive wear causing higher wear rate, the increase in wear scar size with time reduces the contact stresses which gradually enhances the friction and wear performance. This study also looked at the life cycle of HC-600a compressors and compared it to HFC-134a compressors. Extended life economic valuations of annual emissions are given in Table 3. The vales of only 25 years have been presented in Table 3. The values of 15 and 20 years can also be found in the original article [76]. This data implies that the environmental burden is more by using HFC-134a systems than using HC-600a systems.

Table 3. Economic valuation of annual emissions, extended life [76].

Key indicator	HFC-134a	HC-600a
	Year 25	**Year 25**
GWP	32	16
SO_2	35	13
NO_x	7	3.1
PM10	30	13
Total	105	45

A novel pressurized chamber was designed and manufactured [77, 78] to achieve liquid state of refrigerants. The liquid state of refrigerants was required to perform rolling contact fatigue experiments of silicon nitride/steel bearing materials under the influence of HFC-134a and HC-600a refrigerants. The chamber ensured that the refrigerants achieved saturated liquid state which was important to simulate practical conditions and lubrication film. This was to satisfy the boundary conditions as no lubricants were used. A four ball machine consisting of three steel balls and one ceramic ball was modified to incorporate the chamber and to charge the refrigerants. The system was also vacuumed before charging the refrigerant to minimize the effects of atmosphere and air on the tests. It was concluded that the state of the refrigerant affects the wear and the positioning of the pre-induced crack influences the fatigue life.

Rolling contact fatigue testing with refrigerant as lubricant using liquid state HC-600a refrigerant in the modified four ball machine [77, 78] was done by [79]. The rolling direction influenced the fatigue life. The crack initiation and propagation is a function of the microstructure of materials [80]. With an induced ring crack, the residual stresses were relieved at the crack tip in the element.

The setup [77, 78] was also used by [81] to study the relationship between residual stresses and rolling contact fatigue cycles under liquefied HC-600a at different pressures. Interfacial stress distribution of contact spots is independent of the squeezing pressure [82, 83]. It was observed that there is an inverse relationship between rolling contact fatigue and residual stresses as shown in Fig. 12.

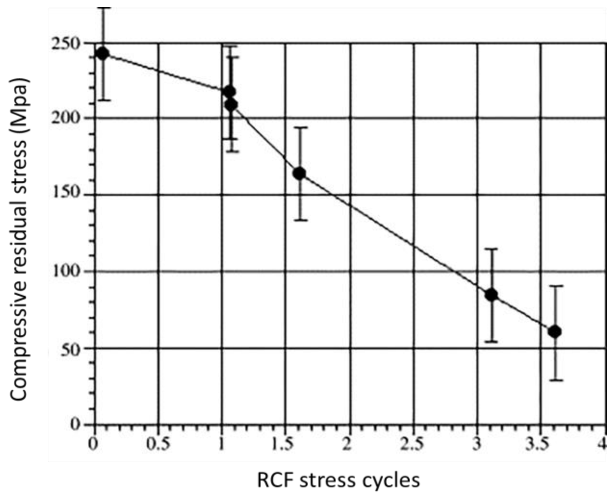


Fig. 12. Compressive residual stress relation to Rolling Contact Fatigue (RCF) stress cycles [83].

The same equipment [77, 78] was used to study; the residual stress relation to the distance from the ring induced crack, the number of stress cycles, the residual stress relation to contact path and the measuring direction [84]. HC-600a was used in liquid state and it was concluded that the compressive residual stresses relieve faster in rolling contact fatigue at elevated contact stress levels. A sub-surface damage in the spall region was observed with reduction in compressive residual stress values.

Controlled pin-on-disk experiments under unlubricated (oil-less) conditions to imitate the wrist pin-connecting rod interface were performed using a High Pressure Tribometer by [85]. Cast iron disks were tested against 52100 steel wrist pins coated with either WC/C or multi-layer WC/C + DLC. HFC-410A, HFC-134a and HC-600a refrigerants were used in this study. HC-600a environment displayed the lowest friction coefficient while HFC-410A environment resulted in the lowest wear. Tests in nitrogen environment were also conducted but the tests resulted in scuffing and the tests had to be stopped. The tribological tests showed that the friction coefficient decreased up to ten times by using coatings. Wear of the pin increases with temperature resulting in the formation of transfer films on the disk from the coating, this caused the steady-state friction coefficient to decrease. The multi-layer coatings have higher hardness which gives these coatings resistance to abrasive wear, this resulted in WC/C + DLC coatings having the least wear. WC/C showed slightly higher friction at lower temperatures, this trend was reversed at higher temperatures.

A pin-on-disk setup comprising of sintered iron disk and 100Cr6 steel pin was used under starved and dry lubrication by [86]. The study involved the investigation of friction and wear performance of 100Cr6/sintered iron pair in HC-600a environment. Sintered iron was treated with and without steam. This study showed that under dry as well as starved lubrication conditions, HC-600a showed adverse effects. In particular for starved lubrication, the wear life of both steam treated sintered steel and untreated sintered steel was reduced to half in the presence of HC-600a compared to air. The increase in wear under HC-600a was thought to be due to change in viscosity and foaming of the oil. Surface analysis also revealed that oxidation under HC-600a was blocked, which caused an increase in weight loss of untreated sintered steel.

Si-rich multifunctional DLC coatings were deposited on 1020 steel and tested against 52100 steel pins using a high pressure pin-on-disk tribometer [87]. Unlubricated friction and wear tests were performed using air, carbon dioxide and HC-600a. HC-600a showed the lowest wear rate and coefficient of friction for both the body and the counter-body. There was a strong presence of graphitic G-band in the spectra of tribolayers formed in the presence of HC-600a which induced its superior tribological performance. The results of the coefficient of friction are shown in Fig. 13.

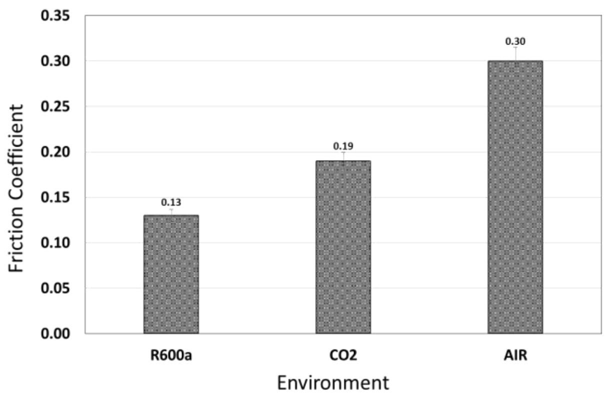


Fig. 13. Average friction coefficient as function of environment [87].

Single-layer WC/C, multilayered WC/C + DLC and TiAlN + WC/C coatings were applied to 52100 steel and Al390-T6 using various contact geometries [88]. The investigation under HC-600a, HFC-134a and HFC-410A atmosphere showed that friction coefficient was the lowest in HC-600a atmosphere while least amount of wear occurred in the case of HFC-410A. HC-600a has the highest percentage of hydrogen atoms per unit volume and hydrogen has a healing effect on hydrogenated DLC coatings in tribological testing, which resulted in lowest friction in HC-600a atmosphere. It was concluded that hard protective coatings offer a great advantage in terms of the tribological performance on interacting surfaces.

A reciprocating ball-on-flat tribometer was used [89] to study the influence of HC-600a and HFC-134a on the friction and wear behavior of multifunctional CrN-Si rich Diamond-like Carbon coatings. The purpose of the study was to investigate the tribo-chemical reactions and the self-lubricating properties of coatings simulating oil-less compressor conditions by using silicon nitride balls against coated flat surfaces. HC-600a presented lower coefficient of friction and lower scuffing durability than HFC-134a. Traces of oxygen were observed in both the cases. Fluorinated compounds were observed on the tribo-layer in the case of HFC-134a. Carbon and silicon were observed in the case of HC-600a. The differences were caused due to the variations in the tribo-chemical reactions caused between the refrigerant gases, the counter body and the multifunctional coatings. It was recommend by this study to use HC-600a where energy saving is required as HC-600a resulted in lower coefficient of friction while HFC-134a was recommend to be used for increased reliability as it resulted in lower wear.

A block-on-ring tribometer comprising of an aluminum alloy block and gray cast iron ring was used [90] to evaluate the lubricity of oil-refrigerant mixtures. Various mineral and POE lubricants were used with HC-290 and HFC-134a. Due to the adverse effects of refrigerants on lubricants, it was concluded that wear in oil-refrigerant mixtures was considerably higher than in oil alone.

6.2 Carbon dioxide (CO_2)

Carbon dioxide (R-744) is an environmentally friendly refrigerant, having zero ODP and minimal GWP. CO_2 is abundantly available in the atmosphere and it can be collected/recycled from air. Besides being environmentally friendly, CO_2 is nonflammable and is in fact used in fire extinguishers to put out fires. It also has good thermodynamic properties and is suitable for a range of applications including industrial heat extraction, shipping vessels, commercial refrigeration systems, etc. The major difference between R-744 and the other refrigerants is its temperature/pressure characteristic and having a low critical temperature. CO_2 systems require special design and a high pressure to operate. The operating pressure requirements make it unsuitable for automobile and domestic applications. An attempt however is being made to design automotive compressors to operate on CO_2.

A scroll compressor to operate on CO_2 was developed [91] for automotive air-conditioning systems. The operating pressure of CO_2 was much higher as compared to HFC-134a, which resulted in low CO_2 scroll compressor thrust bearing reliability and low efficiency due to the large gas thrust. The study concluded to make the compressor lighter and reliable to contribute to its commercialization.

A study [92] was performed to experimentally investigate the physical and chemical properties of CO_2 with various lubricants. The miscibility, viscosity, solubility, lubricity and stability of CO_2

with a number of refrigerant lubricants was studied. The aim of this investigation was to check the compatibility and performance of carbon dioxide with various existing commercial refrigerant lubricants. The lubricants used were Polyalkylene glycol (PAG), Polyol ester (POE), Polyvinylether (PVE) and Polycarbonate (PC). Based on the chemical stability, miscibility and better lubricity under high pressure, PAG was found to be the best lubricant for CO_2 refrigeration systems.

A tribological investigation of 52100 steel disk on 440C bearing steel ball using a reciprocating ball-on-disk tribometer under CO_2 atmosphere was done by [93]. Experiments were conducted in vacuum, air and carbon dioxide atmosphere. The results of the friction coefficient of these experiments are shown in Fig. 14. CO_2 atmosphere resulted in the lowest coefficient of friction.

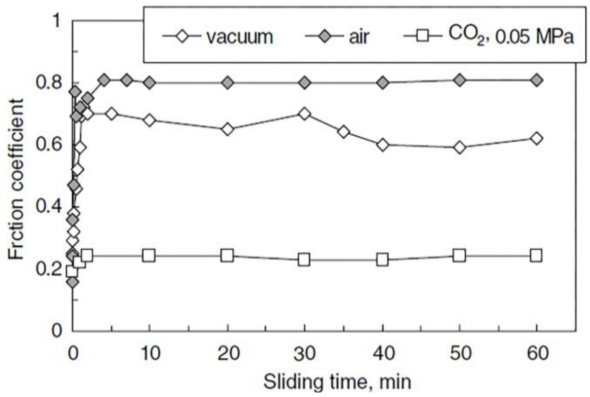


Fig. 14. Lubricant effect of CO_2 on steel couple [93].

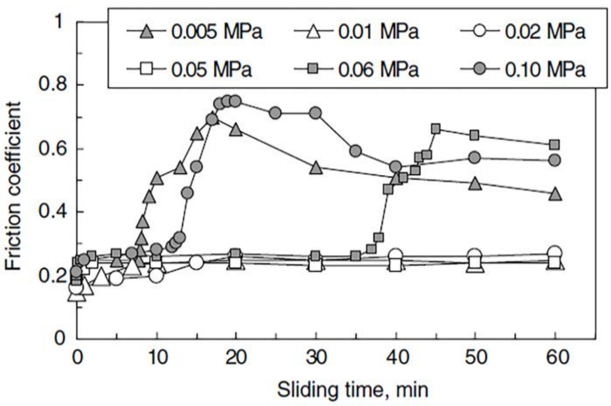


Fig. 15. Effect of CO_2 pressure on lubricating behavior [93].

The effect of the change in pressure of carbon dioxide on the friction coefficient was also studied. The results of this investigation are presented in Fig. 15. It was concluded that carbon dioxide reacted with the disk surfaces and formed carbonate and/or bicarbonate on the disk which played a major role in reducing friction. An optimum pressure in the range of 0.02-0.05 MPa resulted in effective reduction of friction. Lower CO_2 pressures were insufficient to produce carbonate and/or bicarbonates while higher CO_2 pressures produced serious chemical wear.

The tribological performance of carbon dioxide was compared to HFC-134a using 52100 steel pins and Al390-T6 disks under submerged lubricated conditions [94]. PAG and POE were used as lubricants in various combinations with the refrigerants. It was found that the abundance of oxygen while operating in carbon dioxide atmosphere resulted in the formation of oxides which strengthened the top most layer. PAG showed to be the better lubricant with CO_2.

Gray cast iron pins and disks were used in a study [95] to evaluate the tribological performance of CO_2 refrigerant in comparison to HFC-134a under identical operating conditions. PAG lubricants were used in this study. The study concluded by stating that the tribological behavior of the interacting materials using CO_2 was nearly identical to that of HFC-134a.

An ultra-high pressure tribometer was designed and manufactured to study the tribological behavior of carbon dioxide up to 13.8 MPa [96]. Experiments were conducted in the range of 1.4 MPa-6.9 MPa. Boundary lubrication tests were performed using PAG oil with 52100 steel disks against Al390-T6 pins, and unlubricated tests were conducted using gray cast iron pins and disks. Under unlubricated conditions the results at different pressures were similar and under boundary lubrication conditions there was no significant wear. It was also found that increasing the pressure had a positive effect on the coefficient of friction.

A pin-on-disk geometry comprising of Al390-T6 disks and SAE 52100 steel pins was used to study the tribological performance of CO_2 in comparison to HFC-410A [97]. POE and PAG lubricants were used. It was concluded in this study that in comparison to the CO_2 environment, HFC-410A environment resulted in increased disk wear. This was because carbon dioxide promoted a strong oxygenated layer which reduced wear.

A pin-on-disk geometry was used in a high pressure chamber to investigate the friction and wear performance of CO_2 with PAG and POE oils [98]. The pin was made of high speed tool steel and the disk was made of Ni–Cr–Mo gray cast iron. The purpose of the study was to compare the performance of carbon dioxide under PAG and POE oils and examine the influence of pressure variations on friction and wear. The results showed that PAG oil had better lubricity than POE oil in CO_2 refrigerant environment. An increase in pressure increased the solubility of carbon dioxide in case of POE oil which decreased the oil/refrigerant viscosity, whereas variations in pressure had no noticeable effect on the solubility of CO_2 in PAG. As a result the viscosity of PAG was less reduced as compared to POE. The reduction in POE/ CO_2 viscosity was linked to the formation of thin lubricating films on the rubbing surfaces, the thinner film resulted in higher friction and higher wear. In comparison a thick tribo layer was formed when carbon dioxide was used with PAG, the variation in operating pressure did not effect this layer because the solubility of PAG in CO_2 was not effected by pressure which resulted in less friction and wear.

A study involving the use of a pin-on-disk configuration using gray cast iron pins and gray cast iron disks was performed by [99]. The purpose of this study was to investigate the tribological properties of carbon dioxide under a range of pressures and compare its results to air, nitrogen and HFC-134a. Oxide layers were formed under carbon dioxide and oxygen atmospheres, but carbon dioxide showed the best friction and wear results.

Different PTFE-based coatings and DLC coatings were tested using pin-on-disk and shoe-on-disk configurations under air, carbon dioxide and HFC-410A atmospheres [100]. 52100 steel was used as a pin and shoe material, against coated gray cast iron disks. The change of environment showed no significant effect on the tribological behavior of the tested coatings. Overall the use of coatings resulted in a significant improvement in the tribological characteristics. PTFE-based coatings performed better compared to DLC coatings. It was also concluded that the generated wear debris acted as third body lubricants and improved the overall wear performance.

The study [101] compared the tribological performance of POE and PAG lubricants in the presence of carbon dioxide. AI390-T6 disks were used against SAE 52100 pins in a pin-on-disk configuration. It was concluded in this study that formation of carbonate layers are promoted on the surface in the presence of PAG, leading to improvement in the tribological performance.

Al390-T6, gray cast iron and Mn-Si brass disks were used against 52100 steel pins in a pin-on-disk configuration [102]. CO_2 was used as refrigerant with PAG oil. The purpose of the study was to perform a comparative scuffing analysis of metallic surfaces under carbon dioxide environment. Mn–Si brass and gray cast iron performed better than Al390-T6. Unlike Al390-T6 and gray cast iron which failed abruptly in scuffing experiments, Mn–Si brass melted during scuffing which prevented sudden catastrophic failure of Mn–Si brass.

Three different PTFE-based coatings were applied to sintered iron, gray cast iron and Al390-T6 disks to study the significance of tribochemistry on PTFE-based coatings against 52100 steel pins in a pin-on-disk setup in the presence of CO_2 [103]. It was found that the substrate played a major role on the friction and wear properties. $PTFE/MoS_2$ coatings considerably improved the scuffing performance of Al390-T6 substrate. Increase in CO_2 pressure resulted in a thicker PTFE transfer layer which improved the tribological performance.

A pin-on-disk geometry made of gray cast iron was used to study the lubricity effects of carbon dioxide in an ultra-high pressure tribometer [104]. To understand the role of temperature, pressure, carbon dioxide mass and the chemical interaction of CO_2 with gray cast iron on the tribological behavior of CO_2; various regions of CO_2 pressure-temperature (P-T) phase diagrams were studied. The study reported a substantial drop in friction as carbon dioxide approached the gas-liquid transition region on the P-T phase diagram. This indicated a form of super-lubricity. It was also found that increase in CO_2 pressure caused partial transformation of iron oxides into iron carbonates, which positively affected the tribological performance.

A study on the tribological behavior of Mn–Si–brass, Al390-T6 and gray cast iron disks against

52100 steel shoes was performed by [105]. A shoe-on-disk tribometer was used under submerged lubrication condition using PAG oil and CO_2. During the experiments Al390-T6 lost silicon which reduced its structural strength and hardness. Silicon particles have been known to drop out of the aluminum matrix leaving cavities on the surface [106]. Gray cast iron showed the least amount of wear and highest fluid and material retention capability compared to the other materials tested.

7. NEXT GENERATION REFRIGERANTS

The next generation refrigerants are focused on low toxicity, low ODP and low GWP. Focus and attention is also being made on the flammability in the development of next generation refrigerants. The focus on HC has increased after the Kyoto Protocol but due to their flammability, HCs cannot be used in commercial automobile air-conditioners. The future generation refrigerants have to be non-flammable for use and replacement of HFC-134a in the automotive sector. The refrigerant manufacturers have introduced Hydrofluoroolefins and Hydrofluoroethers as potential substitute refrigerants.

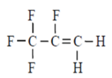
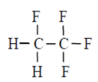
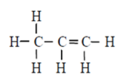
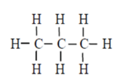
7.1 Hydrofluoroolefins (HFOs)

HFOs are designed to lower the GWP impact that HFCs had while having zero OPD and lower toxicity. One of the most promising future generation refrigerants is 2,3,3,3-Tetrafluoropropene (HFO-1234yf), which is considered a direct replacement of HFC-134a [107]. Although HFO-1234yf has mild flammability, it has been proven to be safe for use as a refrigerant in vehicles [108]. The tribological investigation of HFO-1234yf by various researchers is underway, the work done so far is presented in this section.

A study involving the investigation of ant-seizure characteristics, anti-wear characteristics and chemical stability analysis of saturated and unsaturated refrigerants was done by [109] using disc-on-disc, pin-on-disk and V-block apparatus. Unsaturated refrigerants are those refrigerants that have a double bond in their chemical structure, while saturated refrigerants have only single bonds in their molecular structure. HFO-1234yf is an unsaturated refrigerant having a double bond in its chemical structure. This can cause additional reactions and is expected to influence the tribological performance of the sliding surfaces. This study also used another saturated refrigerant namely, HC-1270 and two unsaturated refrigerants, namely, HFC-134a and HC-290 for comparison. Table 4 shows the molecular structure of these refrigerants. The GWP values, saturation vapor pressures and the refrigeration oils used are also mentioned in Table 4.

The results of the seizure load are shown in Figs. 16(a) and 16(b) respectively. The seizure load of unsaturated HFO-1234yf was larger than saturated HFC-134a and similarly the seizure load of unsaturated HC-1270 was greater than saturated HC-290. The wear results confirmed the superiority of unsaturated refrigerants as compared to saturated refrigerants. The surface analysis revealed substantial amount of fluorine ions on surfaces tested in HFO-1234yf.

Table 4. Refrigerant characteristics and combinations of oil [109].

Series	Hydrofluorocarbon (HFCs)		Hydrocarbon (HCs)	
Refrigerant	HFO-1234yf	HFC-134a	R1270	R290
Molecular structure				
GWP	4	1410	3	3
Saturated vapor pressure at 298 K (MPa)	0.7	0.7	1.2	1.0
Refrigeration oil	Alkyl benzene (AB)		Polyalkylene glycol (PAG)	

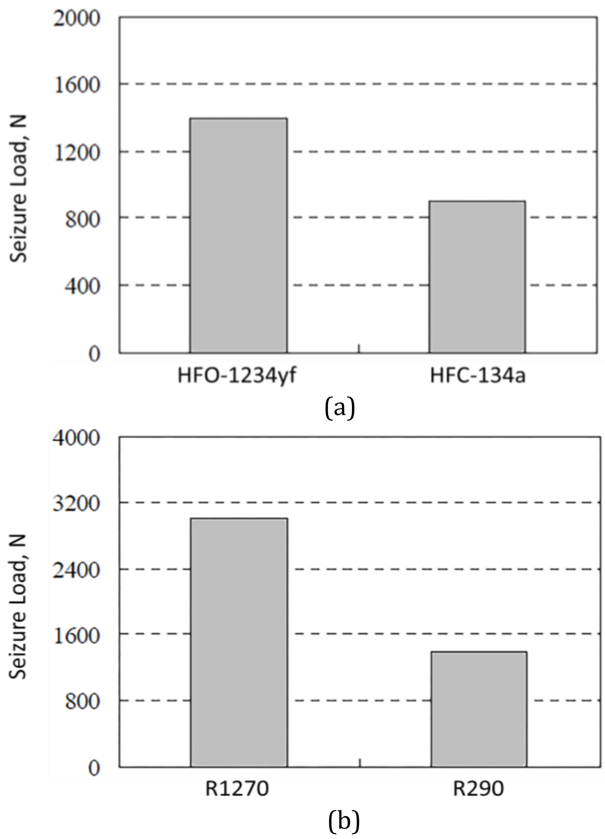


Fig. 16. Seizure load [109].

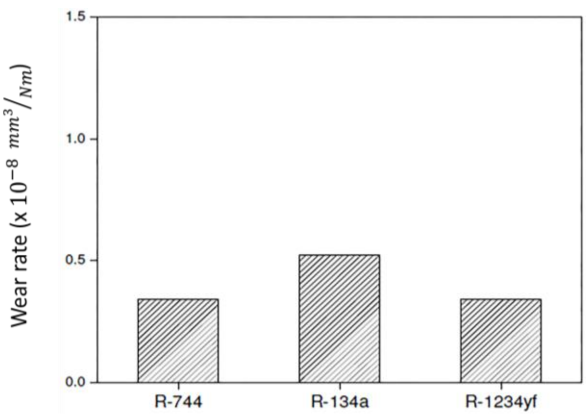


Fig. 17. Calculated average wear rates of a textured pattern in the presence of different refrigerants with PAG lubricant directly applied at interface [110].

A fluoride layer was formed with the adsorption effect of HFO-1234yf and the frictional heat, which helped improve the tribological performance. These results indicate that unsaturated refrigerants perform better than saturated refrigerants from the view point of tribology. The results also show that HFO-1234yf refrigerant has a lot better tribological performance compared to HFC-134a.

A pin-on-disk setup made of grey cast iron pins and disks was used by [110, 111] to experimentally investigate the tribological performance of various unpolished surface textured patters with R-744, HFC-134a and HFO-1234yf under starved lubrication conditions. PAG, POE and mineral oils were used as lubricants and the tests were also conducted on un-textured surfaces under identical conditions. The results of the wear rates by using one of the laser textured geometries with PAG are shown in Fig. 17. HFO-1234yf showed the least amount of wear. The tribological properties of the textured surfaces were affected by the geometrical parameters; depth, diameter and the area density of the micro-dimples. The study concluded that the textured surfaces have a clear advantage over un-textured surfaces.

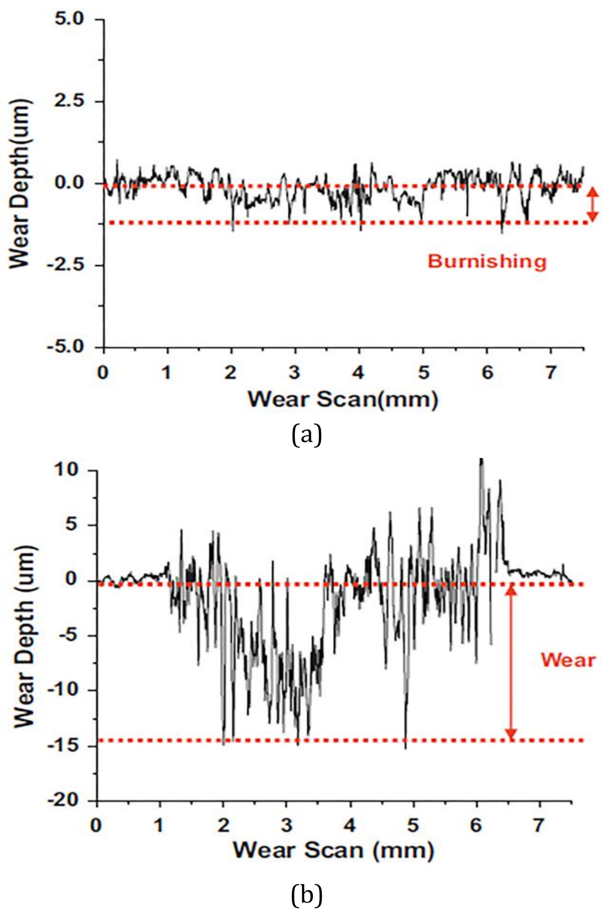


Fig. 18 Profilometric scans of the cast iron wear tracks after experiments in the presence of (a) HFO-1234yf and (b) HFC-134a [112].

A pin-on-disk setup was used [112, 113] to study the tribological effects of HFO-1234yf in comparison to HFC-134a under identical conditions. Two different material pairs were used in this study, namely gray cast iron disk against gray cast iron pin and Al390-T6 disk against 52100 crowned steel pin. No lubricant was used in this study to emphasize the effects of the refrigerants. Wear results of one of the tests are shown in Fig. 18. It can be seen from Fig. 18 that there was less wear in the case of HFO-1234yf. Gray cast iron pairs performed better in this study compared to 52100 steel/aluminum alloy pair for both refrigerants. When used with gray cast iron, HFO-1234yf showed excellent wear performance compared to HFC-134a. The combined effect of the mechanical forces and frictional heating resulted in a tribochemical reaction between the fluorine coming from the unsaturated refrigerant breakdown and the gray cast iron surface. This fluorine containing layer acted as a protective tribo-layer on the top most surface.

Another study to investigate the tribological performance of HFO-1234yf in comparison to HFC-134a was performed by [114]. Gray cast iron pins and disks were used on a pin-on-disk setup. Unlubricated and starved lubrication conditions using PAG oil were simulated in this study. It was seen that HFO-1234yf could sustain twice the load before failing compared to HFC-134a. Fluorine was detected upon surface analysis in the case of using HFO-1234yf. The fluorine containing tribo-layers prevented mental to metal contact and helped sustain extended interface functionality.

The performance of HFO-1234yf was studied with different lubricants, namely, PAG, POE and mineral oils using a gray cast iron pin-on-disk apparatus [115]. Surface analysis of the tested surfaces revealed that fluorine enriched protective surface layers were present by using HFO-1234yf with PAG. PAG showed the best performance with HFO-1234yf compared to POE/HFO-1234yf and mineral oil/HFO-1234yf combinations. PAG has the lowest solubility in HFO-1234yf compared to POE and mineral oil, this allows the lubricant and the refrigerant to preserve their unique properties giving PAG/HFO-1234yf combination the maximum tribological advantage.

52100 steel shoes were tested against different polymeric coated gray cast iron disks in HFO-1234yf atmosphere using a shoe-on-disk tribometer [116]. PAG was used as a lubricant and it was concluded that ATSP/PTFE coatings performed better compared to PTFE-based and Fluorocarbon-based coatings under boundary and dry lubrication conditions. Tribo-chemical benefits were offered by the segregation associated with material enrichment. Oil retention capabilities can improve by the valleys of segregated components that can act as micro-reservoirs under starved lubrication conditions. This results in continuous lubricant supply, which was the case for ATSP/PTFE.

HFO-1233zd which has a boiling point of about 18 °C [117] under normal atmospheric pressure, was used as a lubricant to study film thickness and traction in elastohydrodynamic conditions [118]. This study involved the use of a 52100 steel ball loaded against a glass disk for film thickness measurements using optical interferometry. A ceramic ball was used against steel disk for traction measurements. Numerical and analytical work is also presented in this study for film thickness calculation. The results of the theoretical calculations are compared to the measured film thickness values as well.

7.2 Hydrofluoroethers (HFEs)

Hydrofluoroethers are man-made refrigerants that have been developed to replace CFCs, HCFCs and HFCs. HFEs are nonflammable, odorless, colorless, low toxic and low viscous refrigerants having zero OPD and low GWP. Different variants of HFEs have been developed in the recent past. HFEs have higher boiling points compared to CFCs, HFCs, and HCFCs. HFEs are normally liquid at room temperature and look identical to water. HFO-1234yf has a boiling point comparable to HFC-134a and HFO-1234yf has shown compatibility with synthetic lubricants which were developed for HFC-134a, this makes HFO-1234yf an excellent replacement of HFC-134a. HFEs however have higher boiling points so it is difficult to introduce HFEs into the same thermodynamics cycle and system that was previously used by HFC-134a. Besides having a very low environmental impact, HFEs are nonflammable and possess good thermodynamics properties as coolants [119, 120]. This makes them good candidates for use in various applications.

A study based on the tribological properties of HFE-245mc using a ball-on-sapphire disk-type elastohydrodynamic tester was done by [121]. POE oil having branched chains designed for use with HFC refrigerants was used as a lubricant. HFC-134a and air environment were used as a yardstick to evaluate the performance of this HFE. The chemical formula and various properties of the refrigerants are given in Table 5.

Table 5. Some properties of refrigerants [121].

Refrigerant	HFE-245mc	HFC-134a
Structure	$CF_3CF_2OCH_3$	CH_2FCF_3
Boiling Point (°C)	5	-26
GWP	622	1300
ODP	0	0

The elastohydrodynamic central film thickness was measured using the optical interferometry technique. HFE-245mc/lubricant mixture displayed the lowest film thickness formation capability compared to HFC-134a/lubricant and air/lubricant mixtures.

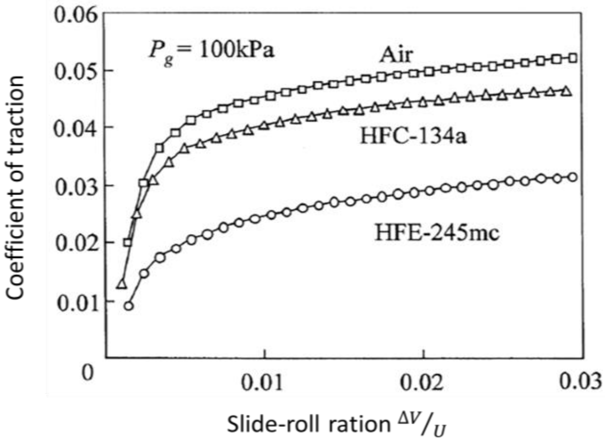


Fig. 19. Traction curves in refrigerants at identical gas pressure [121].

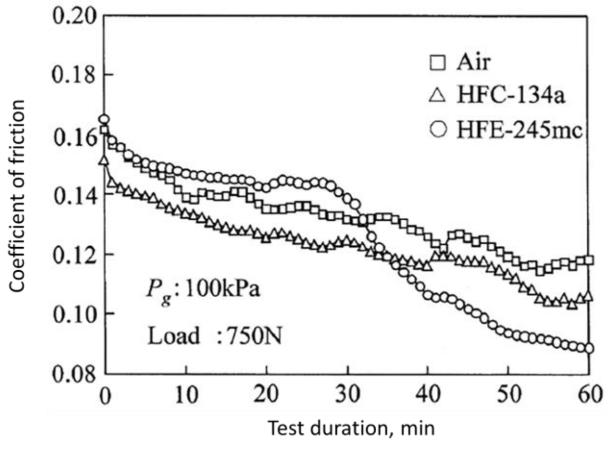


Fig. 20. Boundary friction characteristics in some environments [121].

This was due to the fact that HFC-245mc was more miscible in the lubricant than HFC-134a and air. The high miscibility of HFE-245mc in POE lubricant decreased the viscosity of POE more as compared to HFC-134a and air, this resulted in HFC-245mc having the lowest coefficient of traction as well as shown in Fig. 19. HFE-245mc however displayed the lowest coefficient of friction after running-in of the components was achieved on a block-on-ring tribometer as displayed in Fig .20. HFC-245mc was believed to have reacted with the rubbing surfaces, resulting in the formation of FeF_2 and thick iron oxide films which resulted in good anti-wear performance which resulted in the lowest wear in HFE-245mc atmosphere.

8. CONCLUSION

This review article presents the reported work on the testing of refrigerants from the view point of tribology. An attempt has been made to discuss the major findings while showing selected results from the studies in order not to repeat or present similar results. The similar findings however have been listed in a few cases to highlight the fact that same results were obtained by different studies. The tribological testing of refrigerants from the 1980s to the present day has been discussed.

CFCs and HCFCs refrigerants were chemically formulated in the 1920s to overcome the toxicity and flammability problem of some of the naturally occurring refrigerants. CFCs and HCFCs were used extensively as refrigerants owing to their excellent thermodynamic properties. CFCs and HCFCs showed excellent tribological performance as well. In the presence of CFCs and HCFCs, protective chloride surface films were formed on the interacting surfaces which gave good friction and wear performance. The discovery of the ozone depletion by these refrigerants and the enforcement of Montreal Protocol in 1989 banned the use of CFCs and HCFCs. CFCs have a higher ozone depleting potential than HCFCs, which allowed the use of HCFCs for a longer period of time in comparison to CFCs.

HFCs having zero ozone depleting potential were introduced in the market as replacement refrigerants. They matched the thermodynamic properties of their predecessors but did not show good tribological properties in comparison to CFCs and HCFCs. CFCs and HCFCs were used in compressors with mineral oils as lubricants but HFCs were immiscible and incompatible with mineral oils. New synthetic oils having numerous additives had to be developed for HFCs. In comparison to CFCs and HCFCs, HFCs did not show good friction and wear properties. The fluorine in HFCs did not decompose and form protective surface layers under normal compressor operating conditions. The fluorine in HFCs did decompose at elevated pressures and temperatures and at extreme testing and unlubricated conditions, but was still not as effective as chlorine in CFCs and HCFCs. HFC-134a was adopted as the primary refrigerant for many domestic and commercial applications including uses in fridges, freezers and air-conditioners. Being nonflammable, HFC-134a was also the main candidate for use in automotive air-conditioning systems after CFC-12. The harmful global warming effects of HFCs were realized later after they had been accepted and deployed all over the world. After Kyoto Protocol in 1997, which focused on the causes contributing to global warming, the phase out of HFCs was planned for the coming years.

Natural refrigerants such as hydrocarbon refrigerants also became of interest in 1990s after the limitations on CFCs and HCFCs, but introduction of HFCs did not really allow HCs to be commercialized on a very big scale. This was also due to their high flammability. Now that more emphasis is towards natural refrigerants and HCs are naturally occurring, a strong focus has shifted towards these refrigerates as well. Their flammability is still a concern which prohibits their use in automotive air-conditioning, but HC refrigerants can be used with confidence in domestic and commercial refrigeration and air-conditioning systems. The use of HC refrigerants in heat pumps and fridge and freezer compressors has increased in the recent years. HC-600a has shown better friction and wear properties as compared to HFC-134a as well.

Other than hydrocarbons which inherently have high flammability, carbon dioxide is a good natural refrigerant as well. CO_2 has zero OPD and a GWP value of 1, and it can be collected/recycled from the atmosphere. The physical properties of carbon dioxide unfortunately does not allow it to be used at the operating temperatures and pressures as other refrigerants. The operating pressure has to be much higher for a system based on CO_2 compared to a compressor operating on CFCs or HFCs. Compared to HFC-134a, carbon dioxide has shown good tribological properties by formation of a carbonate layers on the rubbing surfaces. Carbon dioxide which is nonflammable is being investigated for use in automotive air-conditioning applications as well.

Hydrofluoroolefins are newly formulated refrigerants which have zero OPD and lower GWP as compared to HFC refrigerants. HFO-1234yf is considered a direct replacement of HFC-134a, especially in automotive air conditioning applications. The physical and thermodynamic properties of HFO-1234yf are very similar to those of HFC-134a. HFO-1234yf is also compatible with the synthetic oils that were developed for HFC-134a. Unlike HFC-134a, the fluorine in HFO-1234yf has been reported to form protective films on the interacting surfaces with and without lubricants, which improves the friction and wear performance of the system. HFO-1234yf has an unsaturated bond which makes it easier for it to chemically interact with the metallic surfaces and the lubricating oils to improve the tribological performance. The only drawback of HFO-1234yf compared to HFC-134a is that HFO-1234yf has higher flammability than HFC-134a.

Hydrofluoroethers are nontoxic, nonflammable refrigerants which have zero OPD and very low GWP. Their boiling point is much higher than the other commercial refrigerants, this makes them unsuitable for use in the existing fridge, freezer and air-conditioning compressors. However their tribological performance has been reported to be better than HFCs. HFEs have also been reported to form protective tribo-films.

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