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Gaseous Lubricity Additives for Hydrogen Gas

Jie Zhang[a], Bastien Bolle[a], Shouyi Yin[a], Tushar Bera[b], Janet S. S. Wong[a], and Hugh Spikes[a]

[a]The Tribology Group, Department of Mechanical Engineering, Imperial College London, London, UK; [b]Shell Technology Center Houston, Houston, TX, USA

ABSTRACT

There is great interest in using hydrogen as a gaseous fuel in combustion engines to eliminate CO_2 emissions. Unfortunately, hydrogen gas is a poor lubricant for most engineering metals and an effective lubrication solution for pumping and injecting hydrogen is required. This study explores the possibility of additivating hydrogen with a low concentration of a lubricious gas to reduce friction and wear. We find that unsaturated hydrocarbon gas additives form protective carbon-based tribofilms, while gaseous ammonia and amine additives form nitrogen-based films on steel surfaces during rubbing in additivated hydrogen. Gaseous amines are particularly effective in reducing friction and wear, even at concentrations as low as 100 ppm mole/mole. This demonstrates that the addition of a small concentration of lubricious gas is a feasible way to improve the lubricity of gaseous hydrogen.

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Gas-phase lubrication; hydrogen; tribofilm formation; gaseous additives

Introduction

There is growing interest in using hydrogen as a carbon-free gaseous fuel to replace liquid hydrocarbons in crankcase and turbine engines. (*1*,*2*) This gas must be pumped and injected into a combustion chamber, and both pump and injector require effective lubrication to limit friction, wear, and seizure of rubbing surfaces. (*3*–*5*) Unfortunately, as indicated in the following, hydrogen gas is a poor lubricant for most engineering metals, so additional lubrication must be provided, for example, as an oil or grease or as a coating on rubbing parts. (*6*) However, the first of these approaches adds complexity to the component design and use, while coatings must be long-lasting as well as compatible with hydrogen.

This article describes a novel, alternative approach, that of adding small proportions of a chemically active, lubricious gas or vapor species to the hydrogen gas flow in order to provide the required pump and injector lubrication. This approach can be regarded as analogous to the use of dissolved lubricity additives in liquid hydrocarbon fuels but based in the gas rather than the liquid phase.

Background

There has been relatively little previous research on friction and wear in a hydrogen environment, no doubt in part due to safety issues in handling such a combustible gas. In 1939 Bowden and Hughes compared the friction of various metals in oxygen, nitrogen, and hydrogen as well as in vacuum, and found very high friction with nitrogen and hydrogen, similar to that measured in vacuum. (*7*) They noted that the presence of traces of oxygen considerably reduced friction. In 1961, Buckley and Johnson compared the friction and wear of various steel alloys in four gases: dry air, nitrogen, argon, and "forming gas" consisting of 10% H_2 in N_2. (*8*) Friction and wear varied with alloy composition and test temperature but were generally higher in the forming gas than in argon and nitrogen (e.g., 0.8 vs. 0.7 for AISI 52100 at 75 °F). The authors ascribed this to reduction of oxides by hydrogen. Again, a very strong effect of small amounts of oxygen on reducing friction and wear was noted. Very recently the authors of the current article have measured the friction and wear behavior on a range of gases including hydrogen in a sealed reciprocating steel/steel contact. (*9*) They found that hydrogen gave high friction, comparable to that seen with the inert gases, helium, and argon.

In recent years most research on tribological behavior in hydrogen has been carried out by Sugimura and his team at the Research Center for Hydrogen Industrial Use and Storage (HYDROGENIUS) and at Kyushu University in Japan. (*10*–*15*) This has compared the friction and wear behavior of a range of metals in argon and hydrogen and studied the influence of small amounts of oxygen and water on the friction of iron and steel. A difference in frictional response in H_2 between transition and nontransition metals

CONTACT Janet S. S. Wong j.wong@imperial.ac.uk; Hugh Spikes h.spikes@imperial.ac.uk
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was noted, with nontransition metals giving similar behavior in H_2 and argon, comparable to that in vacuum, but some transition metals showing quite different response in the two gases. (*10*) The authors ascribed this to chemisorption of H_2 on some of the transition metals. In the extreme it was found that zirconium and niobium formed hydrides that reduced friction. (*11*) For pure iron, however, friction and wear were quite similar in the two gases. (*12*)

Later work found that for pure iron, trace levels of oxygen and water increased friction and wear, though it was not immediately clear which of these was the main culprit. (*13*,*14*) These were then successfully decoupled, and it was found that trace levels of water at ppm levels reduced the wear rate of iron, though not friction, in H_2, while the combination of water and O_2 increased wear. (*15*)

While there appears to be no previous work on the concept of deliberately using a gaseous additive (apart from O_2 and H_2O) to augment the tribological properties of an otherwise poorly lubricating gas, there has been considerable previous research over many years on supplying additives to a rubbing contact in the vapor phase via a carrier gas, a concept generally known as vapor-phase lubrication (VPL).

The first study appears to have been by Fein and Kreuz (1965), (*16*) who employed a sealed four-ball tester to compare the friction and wear properties of hydrocarbon lubricants both in liquid form and delivered in the vapor phase in different atmospheres. The authors varied the level of oxygen in the atmosphere/carrier gas and concluded that the oxygen to hydrocarbon ratio was a key factor in controlling the tribological performance of the hydrocarbons in the vapor phase.

Interest in VPL grew strongly in the 1980s with the proposed development of adiabatic diesel engines. In principle, such engines offer extremely high efficiency, but they require very high piston and cylinder temperatures, well above the practical operating limit of liquid lubricants. Supply of lubricant as vapor in an inert gas flow was seen as a possible solution to this problem. (*17*–*20*) Initial work looked at obviously chemically active, volatilized species such as phosphate esters, but in 1988 Lauer and Bunting showed that ethylene gas delivered in argon could form tribologically effective carbon-based films on high-temperature rubbing surfaces. (*20*) Interest in the adiabatic crankcase engine subsequently faded, but the concept of vapor-phase lubrication continued to be explored throughout the 1990s (*21*,*22*) and even up to quite recently, (*23*) in the context of high-temperature gas turbine engine lubrication.

Around 2010 another possible application of vapor-phase lubrication was explored, to lubricate microelectromechanical systems (MEMS). (*24*,*25*) Friction and wear pose severe problems in MEMS and constrain their practical use to systems such as switches and positioners that have little or no sliding. It was envisaged that supply of a boundary lubricant in vapor form, either continuously or only during running-in, might alleviate these problems and enable the use of high sliding MEMS.

In recent years, lubricant delivery in the vapor phase has continued to be employed, primarily in fundamental research where it enables study of the tribofilm-forming properties of a single, volatile species, without the complication of a base fluid being present. (*26*–*30*) It has been used to study the tribofilm-forming properties on rubbing surfaces of a variety of different molecular types, including hydrocarbons, (*27*,*30*) alcohols, (*29*) and phosphorus- (*26*) and sulphur-based (*28*) additives. In the last few years there has been particular interest in the role of rubbing itself via mechanochemistry, on tribofilm formation in vapor phase conditions.

Fein and Klaus used a carrier gas consisting of helium or argon with a controlled O_2 content to deliver hydrocarbon vapor, but since then nitrogen has been most widely employed. Exceptions are Lauer et al., who employed argon, (*20*) gas turbine engine work where air was used as the carrier gas, (*21*,*22*) and De Barros-Bouchet et al., who studied vaporized additives in partial vacuum without any carrier gas—a system they termed gas-phase lubrication (GPL). (*26*,*28*) Very recently, Li et al. have compared the tribological behavior in VPL of hydrocarbons delivered using three different carrier gases, N_2, O_2, and a blend of 10% H_2 in N_2. (*30*) They found that saturated and unsaturated hydrocarbons responded differently in these atmospheres, especially with respect to the presence of oxygen. Alkanes and alkene gave low friction and wear in N_2 and N_2/H_2, but only alkene was effective in oxygen. This is consistent with recent findings by the authors of the current article, that in zero- or low-oxygen environments in nitrogen, saturated hydrocarbon molecules react mechanochemically in rubbing metallic contacts to form tribologically beneficial carbonaceous films. (*31*,*32*) However, this reaction is largely prevented when a significant oxygen concentration is present since molecular oxygen reacts with the free radical intermediates involved. It would thus appear that one important aspect of using hydrogen gas is simply, as with nitrogen, to provide an oxygen-free environment in which hydrocarbon and other molecules can react to form tribofilms via free radical processes that would be quenched if oxygen were present.

From the preceding it appears that there have been no previous studies of the tribological response of low concentrations of gaseous additives in a hydrogen gas stream and only one, which employed 10% H_2 in N_2, in vapor phase lubrication.

Methods and materials

This study employs a sealed, reciprocating tribometer, the HPR, supplied by PCS Instruments. This uses the same drive motor, lubricant and disk holder, and ball-and-disk test specimens as the conventional high-frequency reciprocating rig (HFR). However, the reciprocating contact is fully enclosed in a stainless-steel cylinder. The shaft that drives the upper ball holder in reciprocating motion is sealed by two flexible bellows, while the lower disk holder is flexibly mounted and attached to an external force transducer to monitor friction via a thin metal membrane in the cylinder wall. The cylinder wall is also fitted with gas inlet and outlet

ports, a break valve, and a pressure-measuring gauge. The internal free volume of the cylinder is only ~20 mL, and this means that only small volumes of hydrogen are contained, facilitating safe operation. The HPR can be used up to 120 °C and 10 bar pressure, but most tests in the current study were at a controlled temperature of 25 °C and 1 bar pressure. A few were carried out at 100 °C and 1 bar. At the end of each test the wear scar diameter on the ball was measured both along and perpendicular to the sliding direction and the mean value of the two was taken as the wear measurement. Tests employed hardened AISI 52100 steel balls and disks, and test conditions are listed in Table 1. A hard ball on hard disk combination was preferred to the hard–soft configuration used in the ASTM diesel fuel lubricity test (ASTM D6079-18) since hard specimens are more realistic in portraying current fuel injector components.

For the current study, the whole HPR test setup was enclosed in a fume cupboard. Figure 1 shows a photograph of the setup, while Fig. 2 shows a schematic of the gas supply system.

Additive gases were selected on the basis of availability, potential chemical activity, and low odor. At the low concentrations employed, neither combustibility nor formation of undesirable combustion products was considered a significant issue. Most additive blends in hydrogen were supplied as pre-prepared mixtures in lecture bottles with additive concentrations of ~5000 ppm and ~1000 ppm mole/mole (1000 ppm corresponds to a concentration of 4.5×10^{-5} mole/L). The precise compositions of these mixtures were within ±3% of the target concentrations and are listed in Supplementary Information (SI 1). For some additives, concentrations below 1000 ppm were then obtained by combining streams of these pre-prepared blends with a pure hydrogen stream using computer-controlled electronic mixing valves, as illustrated in Fig. 2.

Table 1. Test conditions.

Applied load	1.96 N (200 g), p_{max_Hertz} = 0.82 GPa
Stroke length	1 mm
Stroke frequency	50 Hz (mid stroke sliding speed = 0.16 m/s)
Test duration	30 min
Test temperature	25 ± 1 °C
Disk roughness, Rq	4.8 ± 0.8 nm
Ball roughness, Rq	9.9 ± 1.2 nm
Ball material	AISI 52100 steel
Disk material	AISI 52100 steel
Ball hardness	790 HV
Disk hardness	775 HV

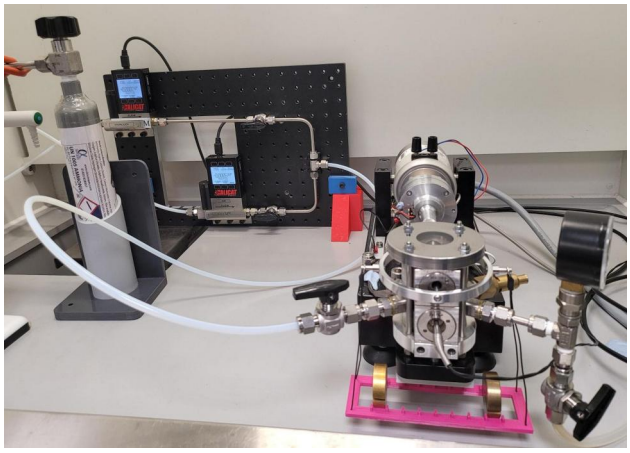


Figure 1. Photograph of test setup within a fume cupboard.

Blends studied are listed in Table 2. All the pre-prepared blends were supplied by a single commercial, US-based supplier that also supplied the hydrogen for further blend dilution. The specified purity of hydrogen used for both blend preparation and further dilution was UHP 99.999%, with less than 1 ppm of $CO + CO_2$, oxygen, water, and total hydrocarbons, and less than 4 ppm nitrogen. The helium gas employed in this study was >99.996%.

For all tests on blends the test chamber was initially purged with pure hydrogen at a flow rate of 4 L/min for 1 min to remove air. Then the test chamber was filled with gas mixture and pressurized to 5 bar. The outlet valve was slowly opened to release the gas mixture, letting the chamber reach ambient pressure. This filling and releasing procedure was repeated five times to ensure testing on the required gas mixture.

In this study, the rubbed tracks on some of the disks were analyzed at the end of tests using x-ray photoelectron spectroscopy (XPS) and/or Raman spectroscopy to identify any tribofilms present. Prior to surface analysis the disks were immediately stored in an N_2 atmosphere after each test.

The worn surfaces were analyzed by XPS. Spectra were acquired on a 50 µm × 50 µm area. The XPS high-resolution spectra were calibrated by using C1s as a reference at 284.8 eV.

Raman spectroscopy was conducted with a lab-built Raman microscope. (*33*) A 532-nm laser and an 20X objective were used to examine the wear tracks on the steel disk. Care was taken to minimize laser damage of the tribofilm while having a reasonable signal-to-noise ratio. Raman spectra were obtained at a laser power of 10 mW, with an integration time of 0.5 s and 10 accumulations.

Results

Additive-free gas

Figure 3 shows friction traces from five repeat tests with additive-free hydrogen. All tests show a high friction coefficient in the range 0.8 to 1.1, with an overall average value of 0.94 ± 0.10. The average wear scar diameter was 496 µm. For comparison, the average friction coefficient and wear scar diameter in helium from two repeat tests under the same conditions were 1.13 and 487 µm, respectively.

Hydrogen with 5000 ppm and 1000 ppm additive

All blends were tested at least twice, and repeats are included in Supplementary Information (SI 2). Figure 4 shows individual, representative traces.

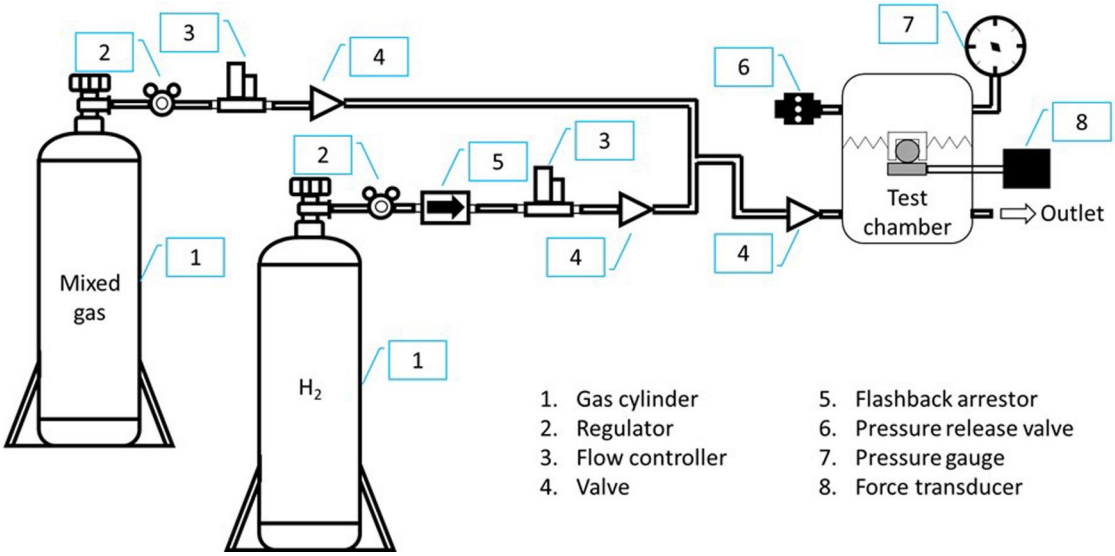


Figure 2. Schematic of gas supply system.

Table 2. List of gases and blends studied.

	Additive	0 ppm (no additive)	5000 ppm	1000 ppm	500 ppm	100 ppm
Helium, He		√				
Hydrogen, H_2		√				
Hydrogen	Ethane, CH_3CH_3		√			
Hydrogen	Ethene, $CH_2{=}CH_2$		√	√		
Hydrogen	Ethyne (acetylene), $CH{\equiv}CH$		√	√		
Hydrogen	Carbon monoxide, CO		√	√		
Hydrogen	Dimethyl ether, CH_3OCH_3		√	√		
Hydrogen	Ammonia, NH_3		√	√	√	
Hydrogen	Methylamine, CH_3NH_2		√	√	√	√
Hydrogen	Dimethylamine, $(CH_3)_2NH$		√	√	√	√

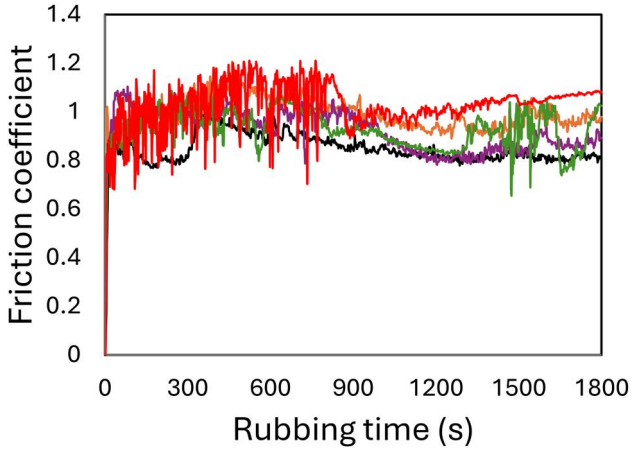


Figure 3. Friction traces from five repeat tests on additive-free H_2.

Figure 4a compares friction traces of all 5000-ppm blends, while Fig. 4b shows an expanded friction axis that differentiates the responses of the more lubricious additives.

It is evident that the addition of ethane to the hydrogen stream does not reduce friction, but that all other additives provide a significant friction reduction. The response of ethene is irregular in that it appears that a friction-reducing tribofilm is formed after about 10 min but is then lost as friction reverts to a value typical of additive-free hydrogen. In four repeat tests on ethene, two showed high friction throughout the test while two showed a transient friction reduction. Carbon monoxide and dimethyl ether are moderately effective, with mean friction coefficients of 0.80 and 0.57, respectively. Ammonia reduces the friction coefficient to ∼0.35. In Fig. 4a the traces of ethyne, methylamine, and dimethylamine appear almost superimposed, but Fig. 4b shows that the two amines have a somewhat lower friction coefficient, around 0.2, compared to ethyne, ∼0.24. The amines also produce low friction almost immediately, while the other additives only reduce friction after ∼100 s of rubbing. Figure 4b also reveals that the friction traces of the amines are not smooth but show short-duration excursions up to ∼0.3.

All additives except for ethane were tested at 1000 ppm, and representative friction traces are shown in Fig. 5. At this lower concentration ethene is ineffective and gives friction similar to that of additive-free hydrogen. Carbon monoxide and dimethyl ether also show little, if any, reduction in friction. Ethyne is ineffective at the start of the test but gives low friction after about 15 min of rubbing. Ammonia is still effective, with a mean friction coefficient of ∼0.34, similar to that seen at 5000 ppm. However, one of three repeats showed higher friction and the average from all tests was 0.47. Methylamine and dimethylamine are both very effective at reducing friction at 1000 ppm concentration.

Figure 6 shows the mean friction coefficient and wear scar diameter for all the 5000 ppm and 1000 ppm blends.

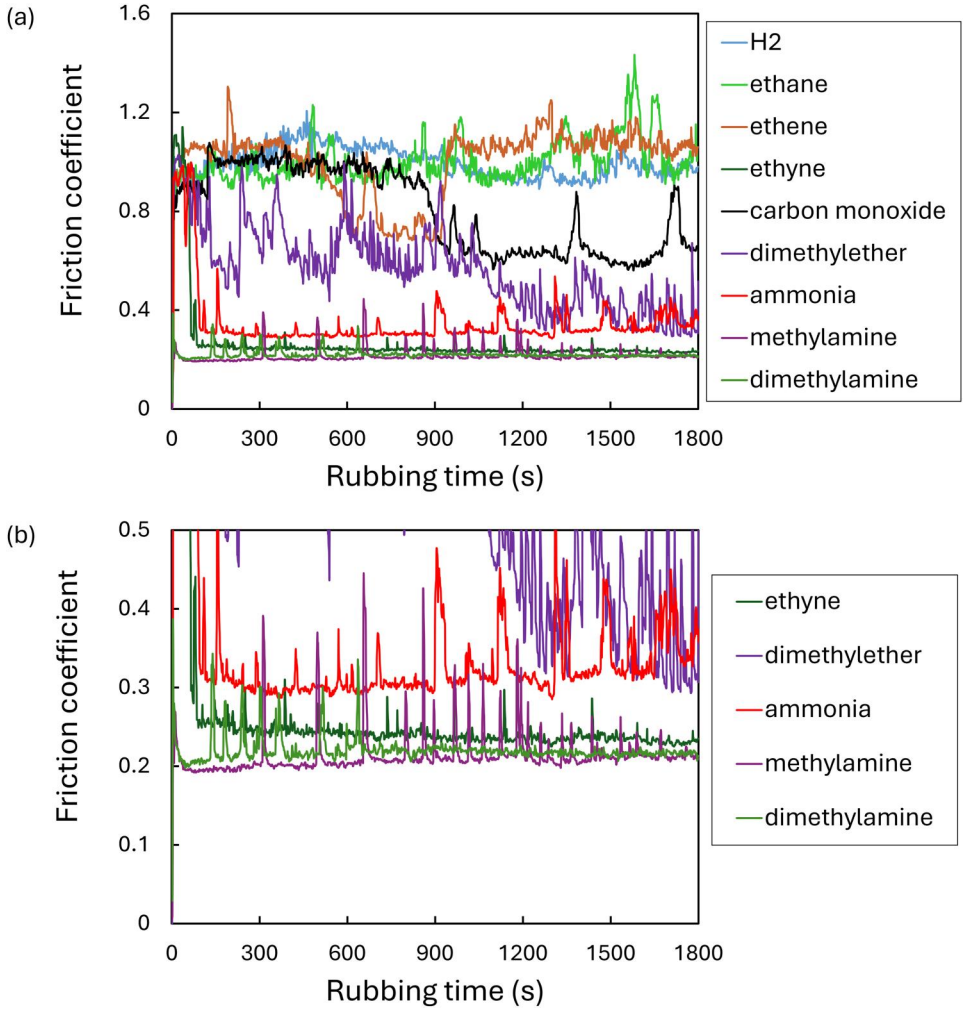


Figure 4. (a) Representative friction traces from tests on 5000 ppm additive in H_2; (b) magnified friction scale to compare lubricious additive response.

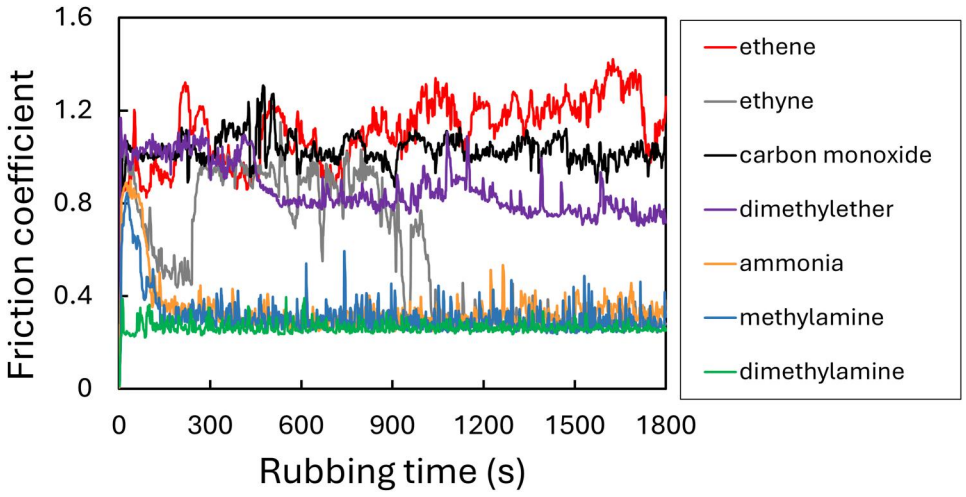


Figure 5. Representative friction traces from tests on 1000 ppm additive in H_2.

Overall, there is good correlation, with those gases that give high friction also giving high wear. Note that ethyne and amine additives are particularly effective in reducing wear. Micrographs of worn disk surfaces can be found in Supplementary Information SI 4. Unlike the worn surface formed in pure H_2, which is quite shiny, the worn surfaces formed in 5000 ppm ethyne and the amines are covered by dark surface films, which are probably responsible for the observed wear reduction. For 5000 ppm NH_3 the worn surface is only partly covered by a dark film (Supplementary Information SI 4), which suggests difficulty in forming or maintaining a surface film and correlates with the intermediate reduction in wear seen with this additive.

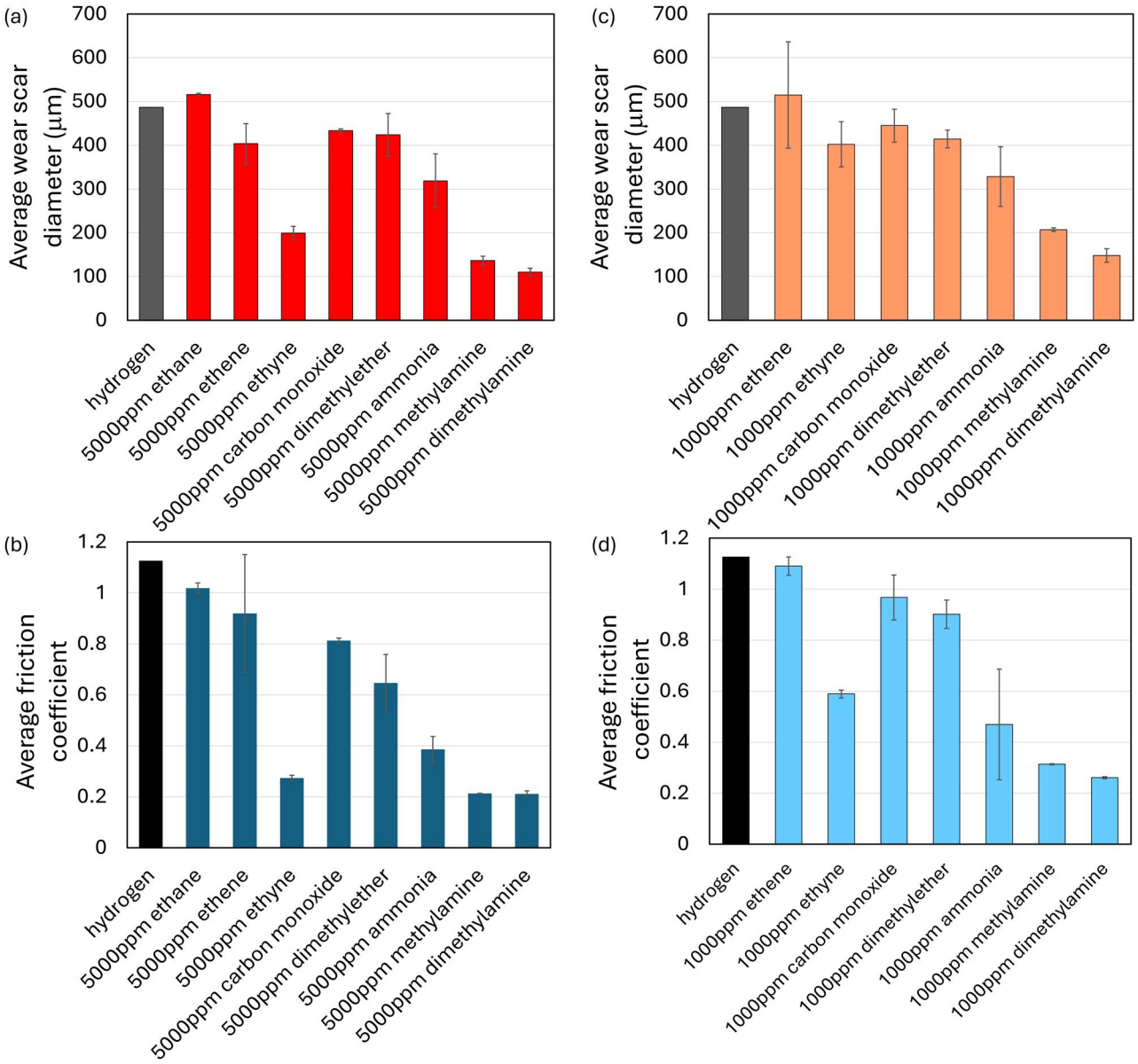


Figure 6. Mean friction coefficients and mean wear scar diameters for (a) and (b) 5000 ppm additives in H_2; and (c) and (d) 1000 ppm additives in H_2.

Effect of varying additive concentration

Ammonia gas additive showed some effectiveness at 1000 ppm so tests were carried out at 500 ppm. However, it was not effective at this concentration, giving a mean friction coefficient of 0.77 and a mean wear scar diameter of 507 μm over two repeats. The amine gas additives that were effective at reducing friction and wear at 1000 ppm were also studied at lower concentrations. Results are shown in Fig. 7. Methylamine continues to be effective down to 500 ppm but is only marginally effective at 100 ppm concentration. Dimethylamine remains effective, with friction coefficient 0.33 and wear scar diameter 200 μm, even at the 100 ppm level.

Discussion

One simplifying feature of gas-phase lubrication is that because there is no liquid lubricant present there can be no formation of a hydrodynamic film in the conditions studied, so the system must operate purely in boundary lubrication. Thus, any reduction (or increase) in friction and wear must result from adsorption of gaseous molecules on the rubbing surfaces, possibly, though not necessarily, followed by their chemical reaction on or with the surfaces, or diffusion into the surfaces. Also, since the predominant atmospheric component in this study is the reducing gas hydrogen, the rubbing surfaces are presumably mainly ferrous alloy metal (Fe and Cr) rather than oxides.

Prior to any tribofilm formation or any wear the contact conditions are severe, due to the very high friction coefficient of ~1.0. This will result in both a high maximum shear stress (820 MPa) and a quite high flash temperature. The maximum sliding speed at mid-stroke is 0.16 m/s and the Hertzian contact radius is 68 μm, giving an initial mean flash temperature of the two surfaces at this point, $\Delta T_{fmean} = 61\mu$ (°C), where μ is the friction coefficient. (*34*,*35*) For a

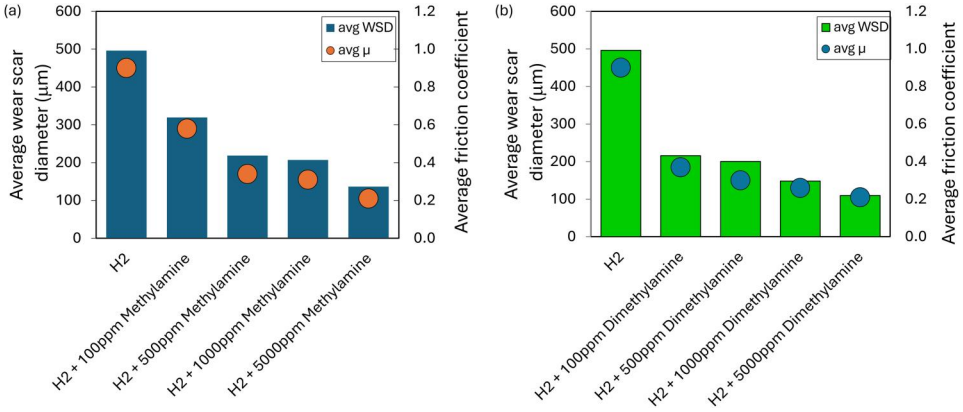


Figure 7. Effect of additive concentration on the friction and wear of (a) methylamine and (b) dimethylamine additives in hydrogen.

friction coefficient of 1.0 this implies a mean flash temperature rise of 61 °C. As wear takes place, the contact diameter will increase, reducing the flash temperature.

For the hydrocarbons tested there is a very clear correlation between lubricity and degree of unsaturation, from ethane, which gives high friction, through ethene, which provides marginal friction reduction at 5000 ppm but none at 1000 ppm, to ethyne, which provides very good friction and wear reduction at 5000 ppm and some at 1000 ppm. This was also found by the authors in a recent study of the friction and wear properties of pure gases using the HPR. (*9*) Many previous studies have shown that both liquid and gaseous hydrocarbons can form carbonaceous tribofilms on rubbing, metallic surfaces to reduce friction and wear. (*32*) This occurs most easily on surfaces that contain catalytic metals (*36,37*) and is also favored in nonoxidizing environments, (*31,32*) as would be provided by hydrogen. It has also been found that unsaturated molecules form such film more readily than saturated ones. (*9,30*) This may be because while saturated hydrocarbons are believed to react to form carbonaceous films at high stresses via free radical processes involving C-C bond rupture, unsaturated hydrocarbons may have an alternative, polymerization route. In a study of vapor-phase lubrication, Argibay et al. found that ethyne/nitrogen mixtures formed carbonaceous tribofilms of thickness 100 to 500 nm on rubbing surfaces at high temperature. (*23*) These films gave low friction but were relatively weak in that they appeared to be worn off when the ethyne feed was interrupted.

Figure 8 shows Raman spectra from a disk rubbed in 5000 ppm ethyne solution. These show clear evidence of D and G bands characteristic of carbonaceous material (*31*) at the sides of the rubbing contact, but no such bands were observed in the center of the track. This suggests that the tribofilm formed by this level of ethyne, although effective at reducing friction and wear, is both very thin and quite weak.

In this study it was found that two gaseous alkylamine additives, methylamine and dimethylamine, provided extremely low friction and wear even at low additive concentrations. Ammonia additive also shows a pronounced friction and wear reduction at the 5000 ppm level, although it was only marginally effective at 1000 ppm. To explore

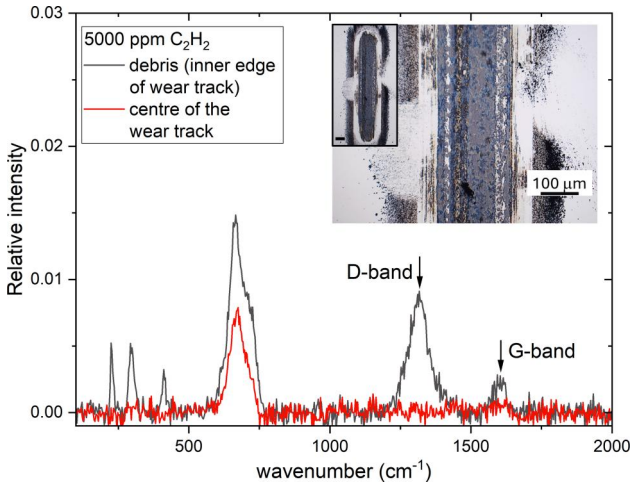


Figure 8. Raman spectra of wear scar formed in 5000 ppm ethyne blend. Inset is a micrograph of the wear scar. The scale bars correspond to 100 μm.

the origins of this, XPS and Raman analyses were carried out on the surfaces of disks at the end of tests using 5000 ppm ammonia, methylamine, and dimethylamine in hydrogen.

XPS survey spectra from worn disk surfaces rubbed in ammonia and the two amines are shown in Supplementary Information SI 3. Figure 9a and b shows XPS N1s spectra taken from the rubbed tracks of tests on the two 5000 ppm amines, while Fig. 9c shows a spectrum taken from a test on 5000 ppm NH_3 in hydrogen. All three spectra show a strong peak at ~400 eV, which can be assigned to adsorbed ammonia or N-H-containing compounds, while the peaks at ~402 eV are believed to be satellite features. (*38–40*) This is consistent with previous observations that fatty amines adsorb readily on steel and their adsorbed mass can be linked directly to friction reduction. (*41*) Note that the relationship between adsorbed mass of fatty amine on steel surface and its concentration in hexadecane is nonlinear, with the rate of increase in adsorbed mass decreasing with increasing concentration. (*41*) A similar mechanism may occur in both oil and gas-phase lubrications. This suggests that the large friction and wear reduction with 100 ppm of amines, followed by only marginal improvement with any further increase in concentration, as shown in Fig. 7, may be driven by physisorption of additives. To explore this

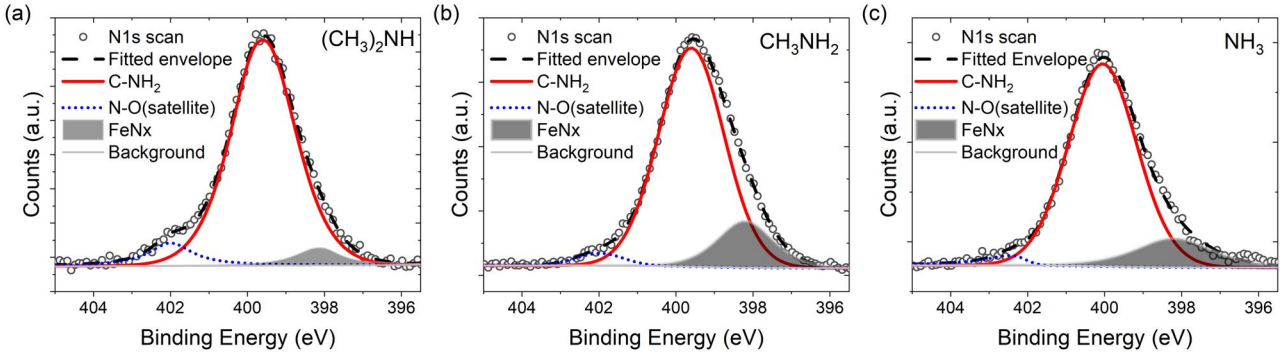


Figure 9. XPS N1s spectra from tests on (a) 5000 ppm dimethylamine, (b) 5000 ppm methylamine, and (c) 5000 ppm ammonia in hydrogen.

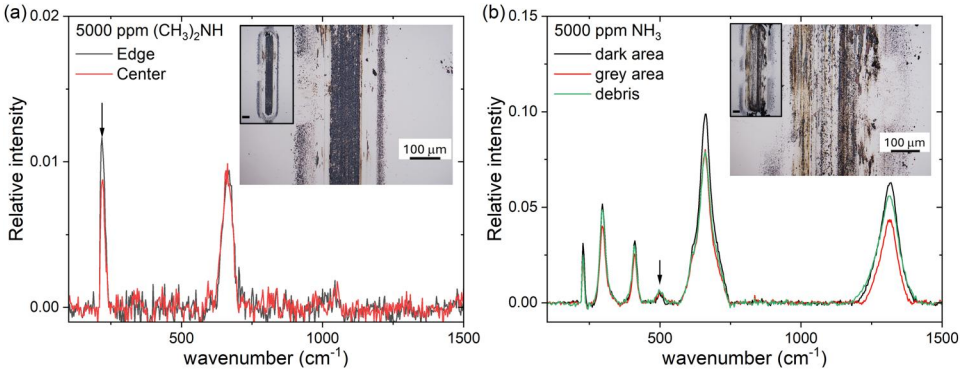


Figure 10. Raman spectra of wear tracks formed in (a) 5000 ppm $(CH_3)_2NH$ and (b) 5000 ppm NH_3 in hydrogen. Insets are micrographs of the wear scars. The scale bars correspond to 100 μm.

further, a few tests were carried out at 100 °C as outlined in the following.

All three spectra show peaks for covalently bonded N, presumably bonded with carbon and/or hydrogen, and also a peak at ~398.1 eV, indicative of a metal nitride. This is labeled as iron nitride but may include chromium nitride since AISI 52100 steel contains about 1% Cr. The finding of nitride is interesting since, while ammonia reacts with steels at high temperature, which is the basis of nitriding, it normally only starts to decompose above 400 °C when suitable catalysts, including iron, are present, and above 800 °C in the absence of catalytic metals. (*42*,*43*) It appears that the severe stress conditions within a rubbing contact cause this decomposition to occur at much lower temperature.

Figure 10a shows Raman spectra from disks rubbed in 5000 ppm dimethylamine blends. They contain a peak at 218 cm^{-1}, which can be assigned to iron nitride (*44*,*45*) and is consistent with the XPS results. The peak at about 660 cm^{-1} can be assigned to iron oxide. Note that spectra taken in different locations in the wear track are similar, suggesting the protective film covers a large part of the track.

Raman spectra in Fig. 10b are from a disk rubbed in 5000 ppm ammonia. A small peak at 500 cm^{-1}, which may be assigned to N-Fe-N linear bond stretching, (*46*) is observed in spectra taken in darker region of the track and debris. However, the intensity of this peak is very low. This suggests that the tribofilm formed in this case is rather weak and may have been removed during rubbing. Alternatively, the formation of nitride may be quite limited. This is consistent with the authors' observations in pure NH_3 (*9*) and may explain the relatively inferior tribological behavior when ammonia is used as an additive compared to the two amines. Other peaks in Fig. 10b are related to iron oxides (227, 296, 410, 660 cm^{-1}). The peak at 1316 cm^{-1} can be due to a second-order scattering process in iron oxide. (*47*)

Table 3. Comparison of friction and wear performance of 1000 ppm of three gases in H_2 at two temperatures (wsd = mean wear scar diameter, μ = mean friction coefficient).

	25 °C		100 °C	
	wsd (μm)	μ	wsd (μm)	μ
1000 ppm Methylamine	207	0.31	376	0.50
1000 ppm Dimethylamine	148	0.26	284	0.38
1000 ppm Ethyne	402	0.59	424	0.74

The relative importance of nitride formation and amine adsorption on friction and wear reduction may be concentration dependent and a few tests were carried out at elevated temperature, both to assess the significance of adsorption and because, in practical terms, gases are likely to experience temperatures considerably higher than 25 °C in injection equipment. Three gaseous additives, ethyne, methylamine, and dimethylamine, were tested at 1000 ppm concentration and 100 °C. Friction and wear results are summarized and compared to values at 25 °C in Table 3, while friction traces are included in Supplementary Information (SI 2b). Friction and wear are all higher at 100 °C than at 25 °C, although the additive gases and especially the amines are still very beneficial. As the friction traces in Supplementary Information show, friction tends to be initially quite high and to stabilize at a lower value after

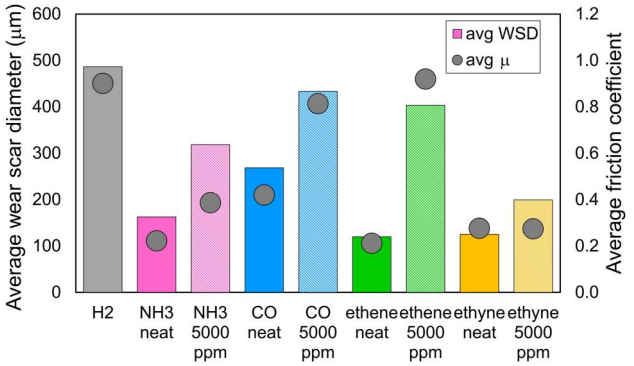


Figure 11. Comparison of the friction and wear properties of neat gases and at 5000 ppm in hydrogen. Neat gas data from Zhang et al. (*9*)

a period of rubbing, as was seen for very low concentrations of the amines (see Supplementary Information SI 2a). This suggests slow formation of a protective tribofilm. Some of the partial loss of friction- and wear-reducing effectiveness at 100 °C may be due to a lower effective concentration, since the concentration of the gases will vary inversely with the absolute temperature due to the ideal gas law, and thus will be only 80% of their value at 25 °C. However, this is not enough to explain the magnitude of the friction and wear increase compared to 25 °C, which suggests that the extent of adsorption of the gases on the rubbing surfaces is an important factor in tribofilm formation.

The friction and wear of some of the gases used as additives in this study were also studied previously as neat gases in HPR tests, (*9*) and it is of interest to compare the behavior of the low-concentration gas blends with the corresponding pure gases under the same conditions. This is shown in Fig. 11 and indicates, as expected, that in almost all cases the gases gave considerably higher friction and wear when present at only 5000 ppm than when they are pure gases. Ethene and CO lost all their ability to reduce friction and wear as a low-concentration additive, but ethyne and to a lesser extent ammonia retained a considerable proportion of their lubricity when present at 5000 ppm.

Conclusions

There is growing interest in using hydrogen as a carbon-free gaseous fuel to replace liquid hydrocarbons in crankcase and turbine engines. This gas must be pumped and injected into a combustion chamber, and both pump and injector require effective lubrication to limit friction, wear, and seizure of rubbing surfaces. This article explores a novel method of improving the lubricity of hydrogen by adding low concentrations of other, surface-active gases. It is found that some such additives, notably ethyne, ammonia, methylamine, and dimethylamine, are effective at reducing friction and wear when added to hydrogen at a concentration of 5000 ppm. The additives methylamine and dimethylamine provide low friction and wear even down to a concentration of 100 ppm. Post test XPS and Raman surface analysis indicate that ethyne forms a carbonaceous tribofilm on rubbed surfaces, while ammonia, methylamine, and dimethylamine form a tribofilm that contains both iron nitride and covalently bound nitrogen atoms, which may stem from physisorption of additives. The study shows that gaseous lubricant additives provide a novel and potentially valuable way to enhance the lubricating properties of hydrogen gas fuel.

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Disclosure statement

Tushar Kanti Bera has a patent pending to Assigned to Shell Global Solutions (US), Inc. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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ORCID

Jie Zhang http://orcid.org/0000-0001-7572-7077
Bastien Bolle http://orcid.org/0009-0008-5382-3744
Shouyi Yin http://orcid.org/0000-0002-4949-8642
Janet S. S. Wong http://orcid.org/0000-0003-2651-7932
Hugh Spikes http://orcid.org/0000-0001-7250-8995

Data availability statement

Data that support the findings of this study are available from the corresponding author upon reasonable request.

References

(1) Falfari, S., Cazzoli, G., Mariani, V., and Bianchi, G. M. (2023), "Hydrogen Application as a Fuel in Internal Combustion Engines," *Energies*, **16**, 2545. doi:10.3390/en16062545

(2) Tiwari, S., Pekris, M. J., and Doherty, J. J. (2024), "A Review of Liquid Hydrogen Aircraft and Propulsion Technologies," *International Journal of Hydrogen Energy*, **57**, pp 1174–1196. doi:10.1016/j.ijhydene.2023.12.263

(3) Welch, A., Mumford, D., Munshi, S., Holbery, J., Boyer, B., Younkins, M., and Jung, H. (2008), "Challenges in Hydrogen Direct Injection Technology for Internal Combustion Engine," SAE Paper 2008-01-2379. SAE International: Warrendale (PA).

(4) Wittek, K., Cogo, V., and Prante, G. (2023), "Development of a Pneumatic Actuated Low-Pressure Direct Injection Gas Injector for Hydrogen-Fueled Internal Combustion Engines," *International Journal of Hydrogen Energy*, **48**, pp 10215–10234. doi:10.1016/j.ijhydene.2022.12.023

(5) Gao, Y. and Lin, M. (2024), "Research on the Performance Characteristics of Hydrogen Circulation Pumps for PEMFC Vehicles," *International Journal of Hydrogen Energy*, **50**, pp 1255–1272. doi:10.1016/j.ijhydene.2023.10.248

(6) Hwang, H. K., Shin, D. H., and Kim, S. J. (2024), "Effect of PVD Deposition Method on Indentation and Friction Wear Characteristics with Hydrogen Embrittlement of CrN Coated

Stainless Steel for Electric Vehicle Hydrogen Valves," *Surfaces and Interfaces*, **48**, 104281. doi:10.1016/j.surfin.2024.104281

(7) Bowden, F. P. and Hughes, T. P. (1939), "The Friction of Clean Metals and the Influence of Adsorbed Gases. The Temperature Coefficient of Friction," *Proceedings of the Royal Society of London*, **A172**, pp 263–279.

(8) Buckley, D. H. and Johnson, R. L. (1961), "Effect of Inert, Reducing, and Oxidizing Atmospheres on Friction and Wear of Metals to 1000 F. NASA Technical Note D-1103," October.

(9) Zhang, J., Wong, J., and Spikes, H. A. (2024), "The Lubricity of Gases," *Tribology Letters*, **72**, 108. doi:10.1007/s11249-024-01911-y

(10) Fukuda, K. and Sugimura, J. (2008), "Sliding Properties of Pure Metals in Hydrogen Environment," *Proceedings of STLE/ASME International Joint Tribology Conference*, IJTC2008, October 20–22, 2008, Miami, Florida, USA, Paper IJTC2008-71210. doi:10.1115/IJTC2008-71210

(11) Murakami, T., Mano, H., Kaneda, K., Hata, M., Sasaki, S., and Sugimura, J. (2010), "Friction and Wear Properties of Zirconium and Niobium in a Hydrogen Environment," *Wear*, **268**, pp 721–729. doi:10.1016/j.wear.2009.11.022

(12) Fukuda, K. and Sugimura, J. (2011), "Influences of Gases on the Tribological Properties of Pure Iron," *Proceedings of STLE/ASME International Joint Tribology Conference*, IJTC2011, October 24–26, 2011, Los Angeles, California, USA, Paper IJTC11-6-1206. doi:10.1115/IJTC2011-61205

(13) Fukuda, K., Kurono, Y., Izumi, N., and Sugimura, J. (2010), "Influence of Trace Water and Oxygen in a Hydrogen Environment on Pure Fe Friction and Wear," *Tribology Online*, **5**, pp 80–86. doi:10.2474/trol.5.80

(14) Fukuda, K., Hashimoto, M., and Sugimura, J. (2011), "Friction and Wear of Ferrous Materials in a Hydrogen Gas Environment," *Tribology Online*, **6**, pp 142–147. doi:10.2474/trol.6.142

(15) Fukuda, K. and Sugimura, J. (2013), "Influences of Trace Water in a Hydrogen Environment on the Tribological Properties of Pure Iron," *Tribology Online*, **8**, pp 22–27. doi:10.2474/trol.8.22

(16) Fein, R. S. and Kreuz, K. L. (1965), "Chemistry of Boundary Lubrication of Steel by Hydrocarbons," *A S L E Transactions*, **8**, pp 29–38. doi:10.1080/05698196508972076

(17) Graham, E. E. and Klaus, E. E. (1986), "Lubrication from the Vapor Phase at High Temperatures," *A S L E Transactions*, **29**, pp 229–234. doi:10.1080/05698198608981682

(18) Gunsel, S., Klaus, E. E., and Bruce, R. W. (1989), "Friction Characteristics of Vapor Deposited Lubricant Films," *SAE Transactions*, **98**, pp 128–135.

(19) Gunsel, S. (1986), *Development and Evaluation of a High-Temperature Lubrication System*, PhD Thesis, The Pennsylvania State University, Ann Arbor, MI.

(20) Lauer, J. L. and Bunting, B. G. (1988), "High Temperature Solid Lubrication by Catalytically Generated Carbon," *Tribology Transactions*, **31**, pp 339–350. doi:10.1080/10402008808981833

(21) Van Treuren, K. W., D. N., Barlow, D. N., Heiser, W. H., Wagner, and Forster, N. H. (1998), "Investigation of Vapor-Phase Lubrication in a Gas Turbine Engine," *Journal of Engineering for Gas Turbines and Power*, **120**, pp 257–262. doi:10.1115/1.2818113

(22) Wagner, M. J., Forster, N. H., Van Treuren, K. W., and Gerardi, D. T. (2000), "Vapor Phase Lubrication for Expendable Gas Turbine Engines," *Journal of Engineering for Gas Turbines and Power*, **122**, pp 185–190. doi:10.1115/1.483193

(23) Argibay, N., Keith, J. H., Krick, B. A., Hahn, D. W., Bourne, G. R., and Sawyer, W. G. (2010), "High-Temperature Vapor Phase Lubrication Using Carbonaceous Gases," *Tribology Letters*, **40**, pp 3–9. doi:10.1007/s11249-009-9514-7

(24) Dugger, M. T. (2011), "Tribological Challenges in MEMS and Their Mitigation via Vapor Phase Lubrication." *Micro-and Nanotechnology Sensors, Systems, and Applications III, SPIE*, Volume 8031, pp 442–452, SPIE Defense, Security, and Sensing: Orlando, FL. doi:10.1117/12.884509

(25) Shen, S. and Meng, Y. (2012), "A Novel Running-In Method for Improving Life-Time of Bulk-Fabricated Silicon MEMS Devices," *Tribology Letters*, **47**, pp 273–284. doi:10.1007/s11249-012-9986-8

(26) De Barros-Bouchet, M. I., Righi, M. C., Philippon, D., Mambingo-Doumbe, S., Le-Mogne, T., Martin, J. M., and Bouffet, A. (2015), "Tribochemistry of Phosphorus Additives: Experiments and First-Principles Calculations," *RSC Advances*, **5**, pp 49270–49279. doi:10.1039/C5RA00721F

(27) He, X., Barthel, A. J., and Kim, S. H. (2016), "Tribochemical Synthesis of Nano-Lubricant Films from Adsorbed Molecules at Sliding Solid Interface: Tribo-Polymers from α-Pinene, Pinane, and n-Decane," *Surface Science*, **648**, pp 352–359. doi:10.1016/j.susc.2016.01.005

(28) De Barros Bouchet, M. I. and Martin, J. M. (2018), "Tribochemistry of n-Alkane Thiols Examined by Gas-Phase Lubrication (GPL)," *Advanced Analytical Methods in Tribology*, ed. M. Dienwiebel and M.-I. De Barros Bouchet, pp 107–128, Springer Nature: London, UK.

(29) Yeon, J., He, X., Martini, A., and Kim, S. H. (2017), "Mechanochemistry at Solid Surfaces: Polymerization of Adsorbed Molecules by Mechanical Shear at Tribological Interfaces," *ACS Applied Materials & Interfaces*, **9**, pp 3142–3148. doi:10.1021/acsami.6b14159

(30) Li, Y. S., Jang, S., Bhuiyan, F. H., Martini, A., and Kim, S. H. (2023), "Molecular Structure and Environment Dependence of Shear-Driven Chemical Reactions: Tribopolymerization of Methylcyclopentane, Cyclohexane and Cyclohexene on Stainless Steel," *Tribology Letters*, **71**, 49. doi:10.1007/s11249-023-01703-w

(31) Zhang, J., Campen, S., Wong, J., and Spikes, H. A. (2022), "Oxidational Wear in Lubricated Contacts—Or Is It?," *Tribology International*, **165**, 107287. doi:10.1016/j.triboint.2021.107287

(32) Zhang, J., Bolle, B., Wong, J. S. S., and Spikes, H. A. (2024), "Influence of Atmosphere on Carbonaceous Film Formation in Rubbing, Metallic Contacts," *Tribology Letters*, **72**, 4. doi:10.1007/s11249-023-01801-9

(33) Garcia Gonzalez, C., Ueda, M., Spikes, H. A., and Wong, J. S. S. (2021), "Time-Resolved Raman Investigation of Low-Friction Film Formation," *Scientific Reports*, **11**, 3621.

(34) Greenwood, J. A. (1991), "An Interpolation Formula for Flash Temperatures," *Wear*, **150**, pp 153–158. doi:10.1016/0043-1648(91)90312-I

(35) Reddyhoff, T., Schmidt, A., and Spikes, H. A. (2019), "Thermal Conductivity and Flash Temperature," *Tribology Letters*, **67**, 22. doi:10.1007/s11249-018-1133-8

(36) Erdemir, A., Ramirez, G., Eryilmaz, O. L., Narayanan, B., Liao, Y., Kamath, G., and Sankaranarayanan, S. K. (2016), "Carbon-Based Tribofilms from Lubricating Oils," *Nature*, **536**, pp 67–71. doi:10.1038/nature18948

(37) Khan, A. M., Ahmed, J., Liu, S., Martin, T., Berkebile, S., Chung, Y. W., and Wang, Q. J. (2023), "Formation of Wear-Protective Tribofilms on Different Steel Surfaces during Lubricated Sliding," *Tribology Letters*, **71**, 63. doi:10.1007/s11249-023-01735-2

(38) Vinod, K. R., Saravanan, P., Sakar, M., and Balakumar, S. (2016), "Insights into the Nitridation of Zero-Valent Iron Nanoparticles for the Facile Synthesis of Iron Nitride Nanoparticles," *RSC Advances*, **6**, pp 45850–45857. doi:10.1039/C6RA04935D

(39) Peng, H., Mo, Z., Liao, S., Liang, H., Yang, L., Luo, F., Song, H., Zhong, Y., and Zhang, B. (2013), "High Performance Fe- and N-Doped Carbon Catalyst with Graphene Structure for Oxygen Reduction," *Scientific Reports*, **3**, 1765. doi:10.1038/srep01765

(40) Wojciechowski, P. and Lewandowski, M. (2022), "Iron Nitride Thin Films: Growth, Structure, and Properties," *Crystal Growth & Design*, **22**, pp 4618–4639. doi:10.1021/acs.cgd.1c01528

(41) Fry, B. M., Chui, M. Y., Moody, G., and Wong, J. S. S. (2020), "Interactions between Organic Friction Modifier Additives," *Tribology International*, **151**, 106438. doi:10.1016/j.triboint.2020.106438

(42) Lucentini, I., Garcia, X., Vendrell, X., and Llorca, J. (2021), "Review of the Decomposition of Ammonia to Generate Hydrogen," *Industrial & Engineering Chemistry Research*, **60**, pp 18560–18611. doi:10.1021/acs.iecr.1c00843

(43) Feng, P., Lee, M., Wang, D., and Suzuki, Y. (2023), "Ammonia Thermal Decomposition on Quartz and Stainless Steel Walls," *International Journal of Hydrogen Energy*, **48**, pp 29209–29219. doi:10.1016/j.ijhydene.2023.04.106

(44) Varga, T., Vásárhelyi, L., Ballai, G., Haspel, H., Oszkó, A., Kukovecz, Á., and Kónya, Z. (2019), "Noble-Metal-Free Iron Nitride/Nitrogen-Doped Graphene Composite for the Oxygen Reduction Reaction," *ACS Omega*, **4**, pp 130–139. doi:10.1021/acsomega.8b02646

(45) Zhang, Y., Xie, Y., Zhou, Y., Wang, X., and Pan, K. (2017), "Well Dispersed Fe_2N Nanoparticles on Surface of Nitrogen-Doped Reduced Graphite Oxide for Highly Efficient Electrochemical Hydrogen Evolution," *Journal of Materials Research*, **32**, pp 1770–1776. doi:10.1557/jmr.2017.138

(46) Gubert, G., Varalda, J., and Mosca, D. H. (2021), "Effect of Wavelength and Fluence in Laser-Induced Iron Nitride Nanostructures," *Journal of Alloys and Compounds*, **856**, 157392. doi:10.1016/j.jallcom.2020.157392

(47) Kumar, P., No-Lee, H., and Kumar, R. (2014), "Synthesis of Phase Pure Iron Oxide Polymorphs Thin Films and Their Enhanced Magnetic Properties," *Journal of Materials Science: Materials in Electronics*, **25**, pp 4553–4561. doi:10.1007/s10854-014-2203-9