Tribology Letters (2024) 72:108
https://doi.org/10.1007/s11249-024-01911-y

ORIGINAL PAPER

The Lubricity of Gases

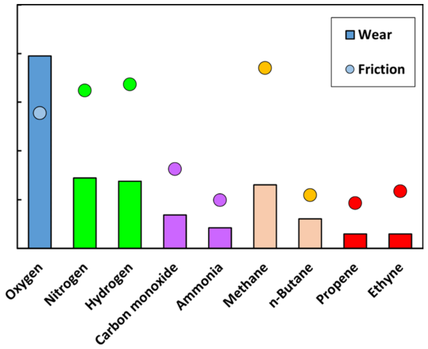
Jie Zhang[1] · Janet S. S. Wong[1] · Hugh A. Spikes[1]

Received: 19 May 2024 / Accepted: 15 August 2024

Abstract

A sealed reciprocating tribometer has been used to study the influence of different gaseous environments on the friction and wear properties of AISI52100 bearing steel at atmospheric pressure and 25 °C. Helium, argon, hydrogen, carbon dioxide and nitrogen all give high friction and wear, suggestive of very little, if any tribofilm formation under the conditions studied. Dry air and oxygen also give high friction, slightly lower than the inert gases, but produce extremely high wear, much higher than the inert gases. This is characteristic of the phenomenon of "oxidational wear". The two gases ammonia and carbon monoxide give relatively low friction and wear, and XPS analysis indicates that this is due to the formation of adsorbed ammonia/nitride and carbonate films respectively. For the hydrocarbon gases studied, two factors appear to control friction and wear, degree of unsaturation and molecular weight. For the saturated hydrocarbons, methane and ethane give high friction and wear but propane and butane give low friction after a period of rubbing that decreases with molecular weight. The unsaturated hydrocarbons all give an immediate reduction in friction with correspondingly low wear. Raman analysis shows that all the hydrocarbons that reduce friction and wear form a carbonaceous tribofilm on the rubbed surfaces.

Graphical Abstract



Keywords Gas lubrication · Ammonia · Carbon monoxide · Friction · Wear · Raman · XPS

1 Introduction

Although most lubricated systems involve the use of a liquid or grease lubricant, there are some systems where the lubricating medium is a gas or vapour. This is the case, for example, in air bearings, gas processing, refrigeration, and when pumping and injecting gaseous fuels into a combustion chamber. In such systems, although coatings may be used to provide some degree of solid lubrication, the ability of the gas itself to provide protective lubricating films is potentially important. Study of the lubricating properties of

---

✉ Janet S. S. Wong
j.wong@imperial.ac.uk

✉ Hugh A. Spikes
h.spikes@imperial.ac.uk

[1] The Tribology Group, Department of Mechanical Engineering, Imperial College London, Exhibition Road, South Kensington, London SW7 2AZ, UK

relatively benign or inert gases such as air, carbon dioxide, nitrogen, and argon is quite straightforward. However, study of combustible or toxic gases such as methane, hydrogen and ammonia is more problematic and this may have constrained investigation into their lubricating properties in the past. To address this, the current paper employs a new, sealed, low volume tribometer to investigate the lubricating properties of a range of different gases of tribological interest.

2 Background

When metallic surfaces are rubbed together in the absence of a liquid, grease or solid lubricant, interactions of the gaseous environment with the rubbing metal surfaces become of paramount importance in determining tribological performance. Such interactions can involve adsorption of gaseous molecules [1–4] and/or their chemical reaction with the surfaces, for example to form metal oxides from molecular oxygen [5, 6] or carbonates from carbon dioxide [7, 8].

2.1 Oxygen

By far the most practically important effect of atmosphere stems from the presence or absence of molecular oxygen. This can be beneficial or deleterious. Thus, several researchers have found that the addition of low levels of oxygen can greatly reduce the high friction and wear observed when ferrous surfaces are rubbed in vacuum or in oxygen-free gases such as nitrogen, argon and hydrogen [2, 4, 9, 10]. It is also widely accepted that the formation of oxide layers on steel provides general protection against adhesive wear [6, 11]. On the other hand, higher wear levels of steel in air (21% O_2) as compared to inert gases have been reported in both sliding and fretting wear [12–14] and ascribed to the formation of easily removed or abrasive oxides. It appears that the impact of molecular oxygen on friction and wear is strongly dependent on steel hardness and on rubbing conditions such as load and the degree of sliding [15].

2.2 Other Gases

Several researchers have studied the properties of nominally oxygen-free gas environments on friction and wear. Most of this work has suggested that H_2, N_2 and inert gases (He, Ar) possess little intrinsic lubricity and impart high friction and wear to sliding steel/steel contacts [10, 16–18]. Some authors have noted slightly lower friction of bearing steel in N_2 than in Ar and proposed that this might originate from the formation of iron or chromium nitride [10, 17]. However, to date surface analysis has failed to detect any such nitrides formed on rubbing steel surfaces from a nitrogen atmosphere. One problem in comparing the friction and wear properties of very low lubricity gases is to be confident that small proportions of O_2 at the sub-100 ppm level, that can be present in some cylinder gases, are not influencing the observed behaviour. In corrosion studies it has been shown that oxide films start to form very rapidly on ferrous surfaces at room temperature at an oxygen partial pressure of 0.01 Pa, which, as a contaminant in inert gas, is equivalent to less than 1 ppm O_2 [5, 19]. Mishina has also suggested that very low concentrations of O_2, N_2 and H_2 in the Pa pressure range can significantly influence friction and wear by adsorbing on rubbing iron surfaces to promote the formation of non-adherent wear debris and thus wear [3, 4].

Several researchers have explored the friction properties of metal surfaces rubbed in a CO_2 atmosphere, both because of the latter's use in some nuclear reactors and due to its role as a refrigerant gas [7, 8, 16–18, 20]. All have found CO_2 to give lower friction and wear than inert gases under some conditions, and surface analysis using XPS has indicated the formation of a ferrous carbonate tribofilm on and around the rubbed steel surfaces.

There appears to have been relatively little work on the influence of gases other than the above on steel-steel friction and wear. Murray et al. studied the friction and wear properties of rubbing contacts in a range of gaseous fluoro- and chlorohydrocarbons and found that some of the latter, notably dichlorodifluoromethane, CCl_2F_2, gave low friction and wear [21]. Surface analysis showed the formation of a chloride tribofilm. Ramirez et al. showed that methane, CH_4, formed a friction-reducing, graphene-like carbonaceous film on rubbing VN-Ni and VN-Cu coated AISI 52100 steel surfaces, but not on uncoated steel, suggesting a catalytically-driven tribochemical reaction [22]. However very recently the authors of the current paper used a sealed tribometer to show that propane gas formed friction-reducing carbon-based films on rubbing 52,100 steel surfaces at room temperature [23]. Research has also been carried out on the ability of a range of carbon-based compounds including carbon monoxide, ethyne and butane, to form tribofilms on nickel and ceramic surfaces, both in the context of vapour phase lubrication and for fundamental study of tribochemical mechanisms [24–26].

While it is very straightforward to design and operate sealed tribometers to study the friction and wear properties of inert gases or relatively benign ones such as dry air and CO_2, where health and safety concerns are minimal, this is not the case when studying combustible gases such as CH_4 and H_2, or toxic ones such as NH_3 and CO. This may have constrained research on the lubricity of these latter gases. However, a low volume, sealed tribometer has recently become commercially available which makes it relatively straightforward to study the friction and reducing properties of a wide range of gases. This paper describes the application of this tribometer to study the ability of a range of nominally pure gases to lubricate rubbing steel-steel contacts.

3 Test Methods and Materials

3.1 HPR Tribometer Tests

This study employs a fully sealed, reciprocating tribometer, the HPR, supplied by PCS Instruments, UK. This reciprocates a 6 mm diameter ball against the flat surface of a stationary disc and employs the same drive motor, test configuration and ball and disc test specimens as the conventional high frequency reciprocating rig (HFR). However, the reciprocating contact is fully enclosed in a stainless-steel cylinder. To achieve this, the shaft that drives the upper ball holder in reciprocating motion and is loaded externally by dead weights is sealed against the cylinder by two flexible bellows. The lower disc 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 and pressure relief valve. The HPR can be used up to 130 °C and 10 bar pressure but in this study most tests were carried out at 1 bar pressure and 25 °C.

The small size of this test rig enables its use in a fume cupboard, while its small internal volume of *ca* 20 ml facilitates the safe study of gases such as hydrogen, methane and ammonia. An additional benefit of this small internal volume is that it enables rapid switching of gases, which can be used to estimate the kinetics of formation and loss of tribofilms, as described later in this paper.

In the current study, gases were supplied to the test chamber at a flow rate of 0.1 L/min using PC-controlled flow controllers, in both pure gas tests and gas-switching tests. For the latter, two flow controllers were connected to two separate gas lecture bottles at one end and to two Swagelok valves at the other. By toggling the Swagelok valves, the gas supply could be switched between the two gases. The two flow controllers were both the MC series from Alicat Scientific, with accuracy at ± 0.6% of reading or ± 0.1% of full scale, whichever is greater.

The overall set-up is shown in Fig. 1 while Fig. 2 shows a schematic of the gas supply system and rig.

The test conditions and characteristics of the ball and disc test specimens are listed in Table 1.

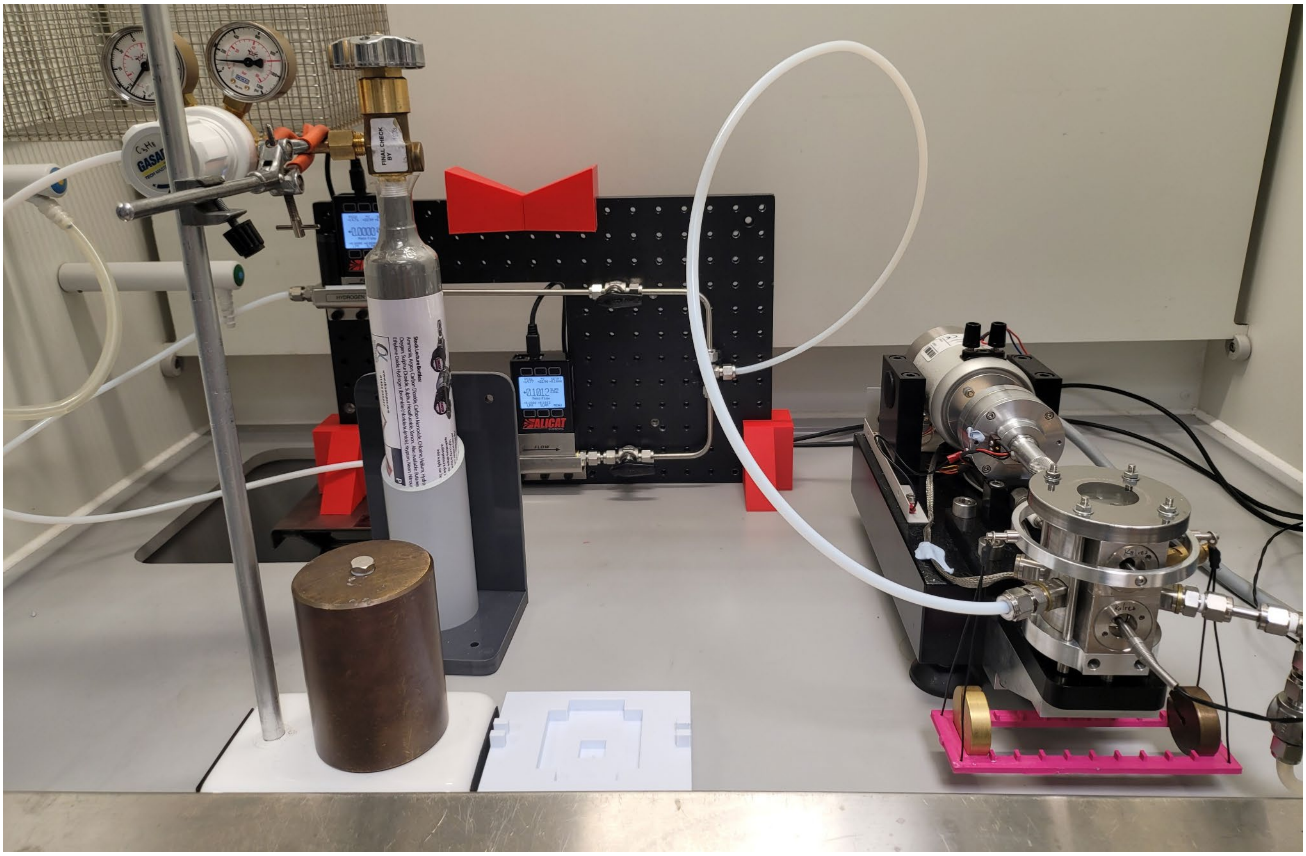


Fig. 1 Photograph of HPR

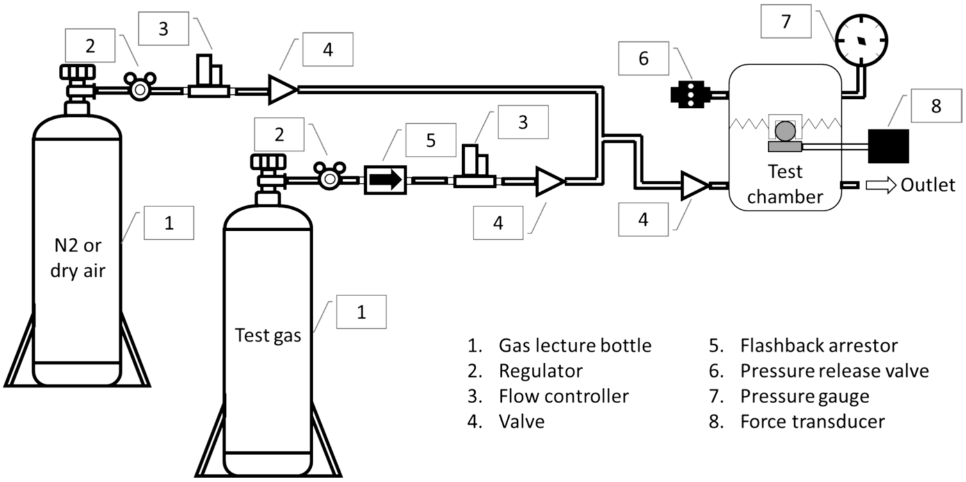


Fig. 2 Schematic of HPR gas supply set-up

Table 1 HPR test conditions

Applied load	1.96 N (200 g), $p_{max}=0.82$ GPa
Stroke length	1 mm
Stroke frequency	50 Hz
Max sliding speed (mid stroke)	0.157 m/s
Test duration in single gas tests	75 min
Test temperature	25 °C ± 0.5 °C
Test pressure	1 bar
Ball roughness, Rq	9.9 ± 1.2 nm
Disc roughness, Rq	4.8 ± 0.8 nm
Ball hardness	790 HV
Disc hardness	800 HV

Although all tests were carried out at 25 °C it is important to consider possible effects of flash temperature rise within the contact during rubbing, especially when friction coefficients are high. Analysis indicated that the mean flash temperature rise in the contact at mid-stroke subject to the conditions in Table 1 and prior to any wear is $\Delta T_{fmean}=61\,\mu$ where μ is the friction coefficient [27, 28].

3.2 Test Gases

The gases tested in this study are listed in Table 2. These were supplied by BOC (Woking, UK) or CK gas (Newtown Unthank, UK). Hydrogen, ammonia and the hydrocarbons

Table 2 Gases tested in this study

Gas		Supplier	Purity
Dry air	N_2, 21% O_2	BOC	
Oxygen	O_2	CK gas	99.999%
Nitrogen	N_2	BOC	> 99.998% O_2 free
Nitrogen	N_2	CK gas	> 99.9999%
Hydrogen	H_2	BOC/CK gas	> 99.99%/> 99.999%
Argon	Ar	BOC	> 99.998%
Helium	He	BOC	> 99.996%
Ammonia	NH_3	CK gas	99.98%
Carbon dioxide	CO_2	CK gas	99.995%
Carbon monoxide	CO	CK gas	99.97%
Methane	CH_4	CK gas	99.9995%
Ethane	CH_3CH_3	CK gas	99.5%
Propane	$CH_3CH_2CH_3$	CK gas	99.5%
n-butane	$CH_3CH_2CH_2CH_3$	CK gas	99.5%
isobutane	$CH_3CH(CH_3)CH_3$	CK gas	99.5%
Ethene	$CH_2{=}CH_2$	CK gas	99.5%
Propene	$CH_3CH{=}CH_2$	CK gas	99.5%
Ethyne	$CH{\equiv}CH$	BOC	> 98.5%

are of interest as possible combustion gases, while carbon dioxide, ammonia and propane are used in refrigeration.

3.3 Surface Analysis Methods

Since the tests were run in dry conditions, post-test solvent cleaning prior to surface analysis was not necessary. For some tests with high wear rate, the disc wear track was partially covered by loose wear debris. In this case a gentle blow using N_2 gas was employed to remove this debris. All the disc specimens were immediately stored in 3 ml glass vials after disassembly from the test chamber. These vials were then promptly purged with N_2 gas to create an inert atmosphere, to avoid contamination and oxidation of the discs before any subsequent analysis.

Confocal Raman spectroscopy was used to analyse disc surfaces from HPR tests. This employed an Alpha 300 RA (WITec, Germany) with a 532 nm laser source, a 600 lines/mm grating with 500 nm blaze and a Zeiss EC Epiplan 20 × objective lens. Spectra were taken with an integration time of 0.5 s for 100 accumulations, giving a total acquisition time of 150 s. The laser power was *ca* 3 mW. Control experiments were conducted to ensure that the obtained spectra were not affected by laser power [29].

Some HFR disc surfaces were analysed at end of test using XPS (Thermo Fisher K-Alpha spectrophotometer). Spectra were acquired from a 50 µm × 50 µm area. The XPS high resolution spectra were calibrated by using C1s as a reference at 284.8 eV.

4 Results

In this section the friction and wear results for each gas are presented and briefly described. Consideration of the origins of the behaviour observed in terms of wear mechanisms and tribofilm formation is deferred to the Discussion section.

4.1 Individual Gases

All gases were tested at least twice and friction traces and wear results for all individual tests are included in Supplementary Information. In the friction graphs below, individual, representative friction traces are shown for clarity.

Figure 3 compares friction coefficient traces in dry air, He, Ar, N_2 and H_2 at 1 bar pressure and 25 °C while Fig. 4 shows traces for dry air, O_2, CO, CO_2 and NH_3. Dry air is included in both graphs for comparative purposes. All gases except for CO and NH_3 show high friction coefficient in the range 0.8–1.2. He, Ar, N_2, He and H_2 give friction coefficient values of *ca* 1–1.2 while dry air and O_2 give slightly lower friction than these gases. N_2 also gives marginally lower friction than the inert gases, especially towards the end of test.

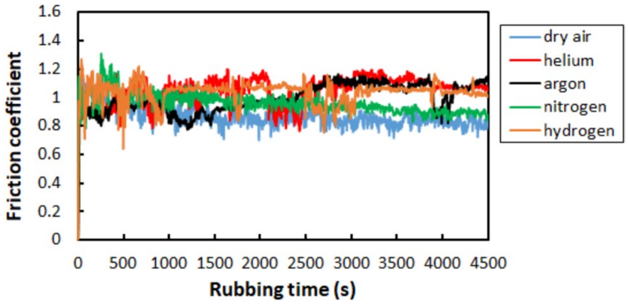


Fig. 3 Friction coefficient traces for dry air, He, Ar, N_2 and H_2

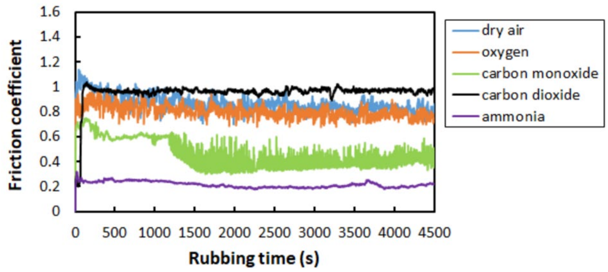


Fig. 4 Friction coefficient traces for dry air, O_2, CO, CO_2 and NH_3 at 25 °C

Carbon monoxide and ammonia give much lower friction than the other gases shown. The trace for CO is very noisy and this was also seen in two repeat tests (see Supplementary Information).

Figures 5 and 6 show friction coefficient traces from tests with saturated and unsaturated hydrocarbon gases respectively. Note that the friction scale in Fig. 6 is different from that in Figs. 3, 4, 5. For the saturated hydrocarbons, methane and ethane show high friction, similar to N_2, H_2 and the inert gases, suggesting that they do not form effective tribofilms under these conditions. There is however some indication of a slight reduction of friction for ethane in the later stage of the test and this was also seen in a repeat test. Propane shows a pronounced friction reduction to a quite low value after about 30 min rubbing and this was also seen in a repeat test. n-butane and isobutane both show very rapid friction reduction to values of ca 0.2. These friction drops occur between 1 and 6 min after the start of a test.

The unsaturated hydrocarbons, ethene and propene show low friction coefficients of *ca* 0.2 throughout the test, with no initial high friction at the start as seen with the butanes. Ethyne gives slightly a higher friction coefficient of *ca* 0.27 but again this low friction is established at the start of the test, indicative of very rapid tribofilm formation.

Figure 7 summarises friction and wear results from all tests, showing the average values from all repeats for each gas. There is generally good correlation between friction and

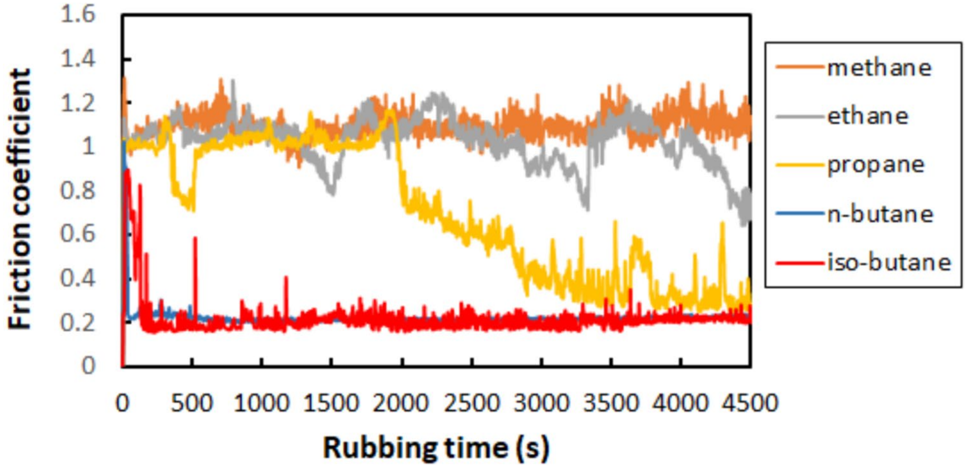


Fig. 5 Friction coefficient traces for five saturated hydrocarbon gases

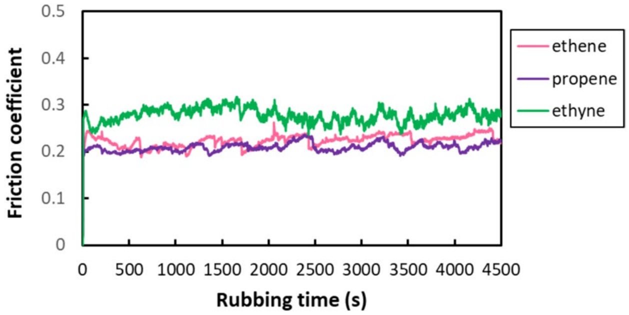


Fig. 6 Friction coefficient traces for three unsaturated hydrocarbon gases

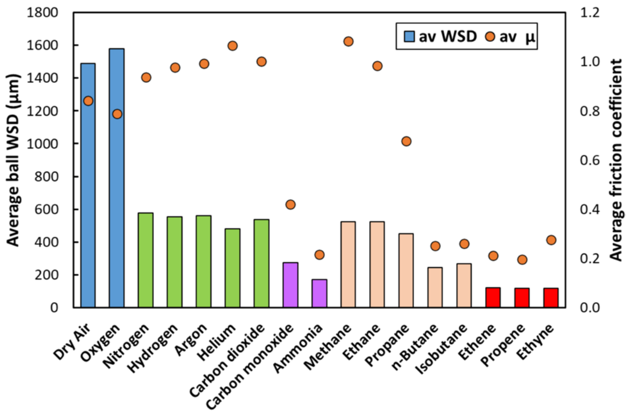


Fig. 7 Summary of average wear scar diameter (WSD) on the balls and friction coefficient, (µ), results for all gases tested

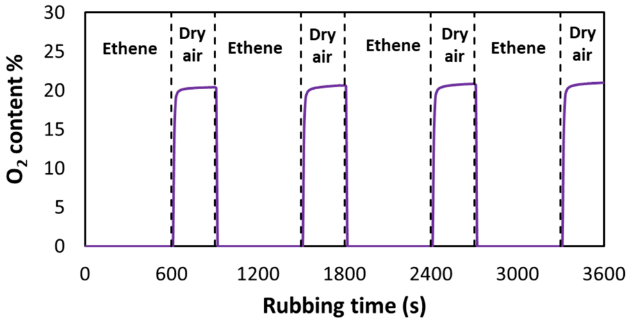


Fig. 8 Rate of variation of O_2 content during switch test between ethene and dry air

wear reduction, except for dry air, oxygen and propane. Dry air and oxygen show high friction, slightly lower than the inert gases, but extremely high wear, much greater than for the inert gases. This is further discussed later in the paper. Propane shows intermediate friction but wear that is only slightly lower than the inert gases. This reflects the fact that friction reduction, presumably originating from tribofilm formation, occurs part-way through the tests. This reduces the mean friction, but it is likely that most of the measured wear occurred prior to formation of a protective tribofilm.

4.2 Switching Gases

Some tests were carried out in which two supplied gases were switched periodically to investigate the kinetics and durability of tribofilms using the set-up shown schematically in Fig. 2. To illustrate the rate at which gases were exchanged, Fig. 8 shows how O_2 level varied when switching between ethene and dry air, with O_2 level being monitored using a fast response oxygen sensor in the outlet flow. Gas exchange was rapid, matching the gas supply rate.

Figure 9 shows two repeat tests in which the atmosphere was switched between propene and dry air. Propene gives low friction, as seen previously in Fig. 6, but friction then rises as soon as dry air is introduced, suggesting very rapid loss of tribofilm. Then, when propene replaces dry air, friction reduces once more, indicating rapid tribofilm reformation.

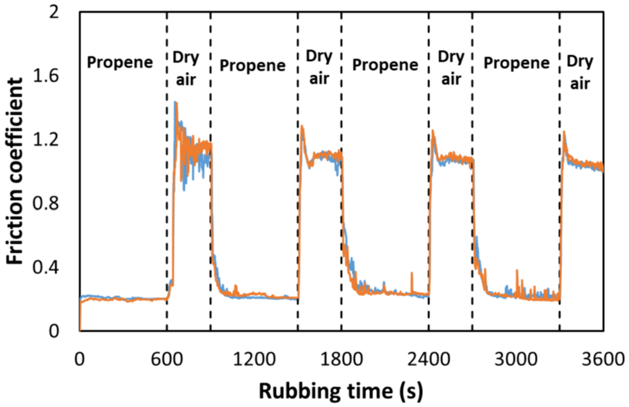


Fig. 9 Friction coefficient variation during switching between propene and dry air

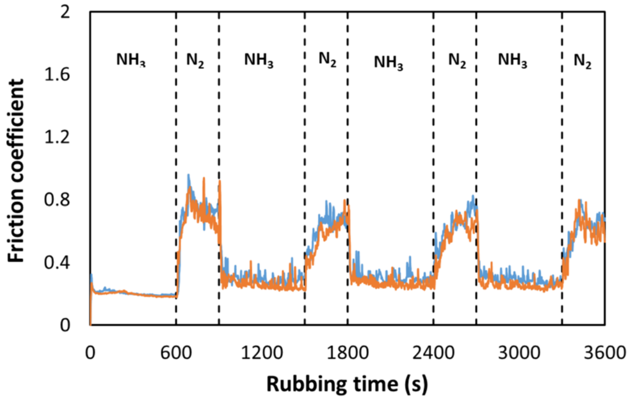


Fig. 11 Friction coefficient variation during switching between ammonia and nitrogen gas

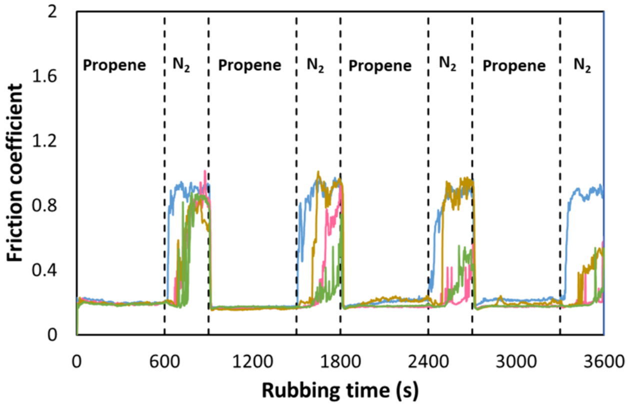


Fig. 10 Friction coefficient variation during switching between propene and nitrogen gas

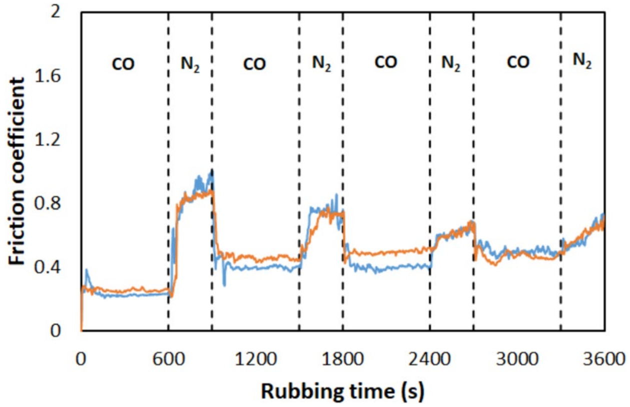


Fig. 12 Friction coefficient variation during switching between carbon monoxide and nitrogen gas

It is not clear from the tests shown in Fig. 9 whether the loss of tribofilm and consequent rise in friction in air occurred because the film was weak and thus easily removed by rubbing once no propene was available to regenerate it, or whether the oxygen in air had a specifically detrimental chemical effect on the propene tribofilm. To assess this, tests were carried out switching between propene and nitrogen as shown in Fig. 10. The results were quite variable over time, so four repeats were carried out. It is evident that friction rises when the propene atmosphere is replaced by nitrogen, implying that the tribofilm formed by propene is initially quite weak and being continually formed and removed. It is also evident that friction rises more slowly when propene is replaced by nitrogen than when it is replaced by air, indicating that there is also a direct chemical contribution to tribofilm removal by oxygen, as suggested from in-contact Raman studies [23]. Most striking is that in three of the four repeats carried out, the tribofilm appears to become stronger over rubbing time in propene since friction takes longer to increase and eventually only partially increases when the atmosphere is switched to nitrogen.

Tests were also carried out switching between NH_3 and N_2 and between CO and N_2 to assess the strength of the films formed by these gases. Figure 11 shows results for switching between NH_3 and N_2. During the first switch to N_2 the friction rises sharply, suggesting that the film is rapidly removed. However, during subsequent switches to N_2 the film is lost more slowly, implying that it is becoming more resistant to removal, as was seen with propene.

Figure 12 shows friction traces from tests in which CO and N_2 gases were switched. Friction rises rapidly after switching to $N_{2,}$ indicating loss of CO-originating tribofilm. However, during each subsequent switch to N_2 the friction stabilises at a lower value, possibly suggesting that less and less low friction tribofilm is being removed by rubbing in N_2. However, the friction in a CO atmosphere appears to increase slightly during successive switches.

Other switching results are included in Supplementary Information.

5 Discussion

5.1 Low Lubricity Gases He, Ar, H_2, N_2, CO_2

He, Ar and H_2 all showed high friction coefficients in the range 0.9–1.2, indicative of little or no lubricity. This is in accord with previous studies [1, 10, 16, 17]. Some previous work has suggested that H_2 might give higher friction than the inert gases because it might reduce any iron oxides present [10], but this cannot be concluded from the current study. N_2 appears to give slightly lower friction than the inert gases, in the range 0.8–1.0. Previous researchers have suggested that N_2 might react with steel during rubbing to form a nitride and that this could be responsible for some friction reduction [10, 17]. XPS was therefore carried out on HFR discs from tests with N_2. These did show very slight traces of nitrogen compounds at *ca* 400 eV within the rubbed track, but similar traces were also seen on fresh discs and so are not believed to indicate a tribofilm. To assess possible effects of traces of O_2 or H_2O in the cylinder gases, two types of cylinder N_2 were used, highly pure N_2 N6.0 and also "N_2 oxygen free" from BOC. However, both gave similar friction behaviour to that shown in Fig. 3.

Figure 4 shows that CO_2 gives high friction coefficient of *ca* 1.0, comparable to that of the inert gases. This is contrary to some previous work. Nunez et al. found that CO_2 reduced friction of grey cast iron but that this only occurred close to the gas–liquid transition, i.e. at high pressure and/or low temperature [8]. At atmospheric pressure they found no friction reduction, in agreement with the current work. Wu et al. obtained low friction of 52,100 steel in CO_2 and related this to the formation of carbonate and bicarbonate [7]. However, their study was at considerably lower speed (lower frequency and longer stroke length) than the current work. Velkahvr et al. used a reciprocating rig at conditions quite similar to the current study and found that CO_2 gave variable friction, ranging between 0.8 and 0.2, with rapid transition between the two values suggesting loss and reformation of a tribofilm. They also detected a carbonate or bicarbonate tribofilm using XPS [17, 21]. It appears that CO_2 may have very marginal lubricity that depends critically on the conditions studied.

All five gases show high wear, in the range 500–600 µm in wear scar diameter, with helium giving somewhat lower wear than the others. This might originate from very small levels of impurity in the gas since the specification for the He used was only $O_2 \leq 7$ ppm, $H_2O \leq 5$ ppm.

5.2 Dry Air and O_2

Dry air and O_2 gave high friction coefficients in the 0.8–0.9 range, slightly lower than the five gases above, but they both produced extremely high wear, much larger than the wear seen with all other gases. Indeed, this wear was so large that the final wear scar diameters exceeded the reciprocating stroke length, so towards the end of tests the contacts may have been operating in fretting rather than sliding wear mode [30]. Pure O_2 gas gave slightly higher wear and slightly lower friction than dry air (21% O_2).

This very high wear probably represents classical oxidational wear, where, in dry conditions, iron oxides are formed during rubbing and then removed by mechanical action—effectively corrosive-abrasive wear. Such wear in air was first identified in the 1950s [12] but the concept of oxidational wear was formalised and modelled in a series of papers by Quinn from the 1960s [31–34]. Quinn's oxidational wear model is based on the assumption that wear occurs at high temperatures generated by rubbing, but in the current work the calculated mean flash temperature at mid-stroke is relatively low (*ca* 60°C at a friction coefficient of 1.0), implying an initial total surface temperature of less than 100 °C. Of course, Quinn's oxidational model preceded knowledge of, and thus takes no account of, the possibility of mechanochemical effects.

Although the wear is much higher when O_2 is present than in oxygen-free N_2, the friction coefficient is similar at *ca* 0.8. This might be because, although wear is dominated by oxide loss, friction is dominated by adhesion between metallic asperities. Alternatively, this friction coefficient may reflect the actual value of friction coefficient of iron oxide on iron oxide. To explore this a test was carried out using haematite (Fe_2O_3) HPR ball and disc in helium. This is shown in Supplementary Information and indicates that dry Fe_2O_3/Fe_2O_3 gives a friction coefficient approaching 1.0. Thus the friction measured when steel surfaces are rubbed in dry air or oxygen may simply reflect the value of iron(III) oxide against iron(III) oxide, although it may equally well originate from iron/iron asperity adhesion; or quite possibly a combination of both.

A key difference between an oxygen-free and an oxygen-containing atmosphere may simply be that in the former, many metallic wear particles remain adhered to the rubbing surfaces, suppressing material loss, while in the latter, as ferrous oxide they do not adhere strongly and thus are easily dislodged from the rubbing surfaces, so enabling high rate of material loss.

5.3 Lubricious Non-hydrocarbon Gases

In Fig. 4 it can be seen that the two gases, NH_3 and CO, give much lower wear than the other non-hydrocarbon gases studied, indicating that these form lubricious tribofilms on the rubbing surfaces. Little previous research has been carried out on the friction and wear of these gases although Blanchet et al. have suggested that blends of CO with H_2 may generate carbonaceous tribofilms on rubbing ceramic surfaces at high temperature [25].

From the gas-switching results in Figs. 11 and 12 it is evident that the initially-formed tribofilms are not very strong in that they are removed by rubbing in N_2. However, for NH_3 the tribofilm appears to become more slowly removed after several switching cycles, while for CO the film seems to become fully resistant to rubbing over time.

To explore the origins of this friction reduction, XPS and Raman surface analysis were carried out on the rubbed tracks of HPR discs at the end of tests in the two gases.

XPS survey spectra from a fresh steel disc surface and from rubbed tracks tested in NH_3 and CO are shown in Supplementary Information. A strong nitrogen signal was only observed from the sample rubbed in NH_3 and its high resolution N1s and C1s XPS spectra are shown in Fig. 13. Corresponding spectra from a fresh, unrubbed, disc surface are included in Supplementary Information. The N1s spectrum shows evidence of iron nitride (397.94 eV and 398.67 eV) as well as adsorbed ammonia (400 eV) [35–37]. Interestingly, the C1s spectrum contains peaks from C–N and C=N. This supports the interpretation that the tribofilm formed in NH_3 contains nitrides. The peak from C–C bonds most likely originates from adventitious carbon. It should be noted that a Raman spectrum of this worn surface did not contain an obvious nitride-related peak, probably because the tribofilm is very thin. This may explain the difficulty in identifying this film in previous studies.

The XPS spectrum obtained from the disc tracks rubbed in CO (Fig. 14) contains a –C–C– peak from adventitious carbon. The peak at 286 cm^{-1} may corresponds to adsorbed CO or adventitious carbon [38]. There are also peaks from polar carbon and carbonate moieties. This is consistent with the literature, where metal carbonate has been detected in tribofilms formed on steel surfaces rubbed in CO_2 [7, 20].

5.4 Saturated Hydrocarbons

Figures 5 and 7 showed the influence of five saturated gaseous hydrocarbons on friction and wear and indicates that their lubricity increases markedly with molecular weight. Methane and ethane give friction and wear values similar to

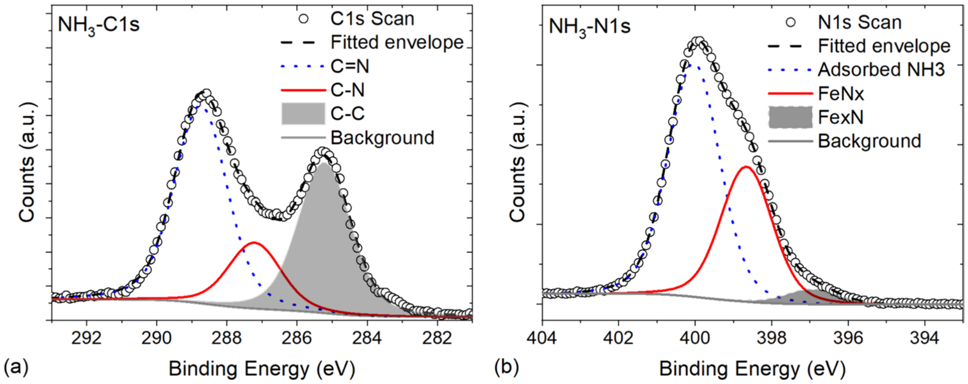


Fig. 13 **a** C1s and **b** N1s spectra from disc track rubbed in NH_3

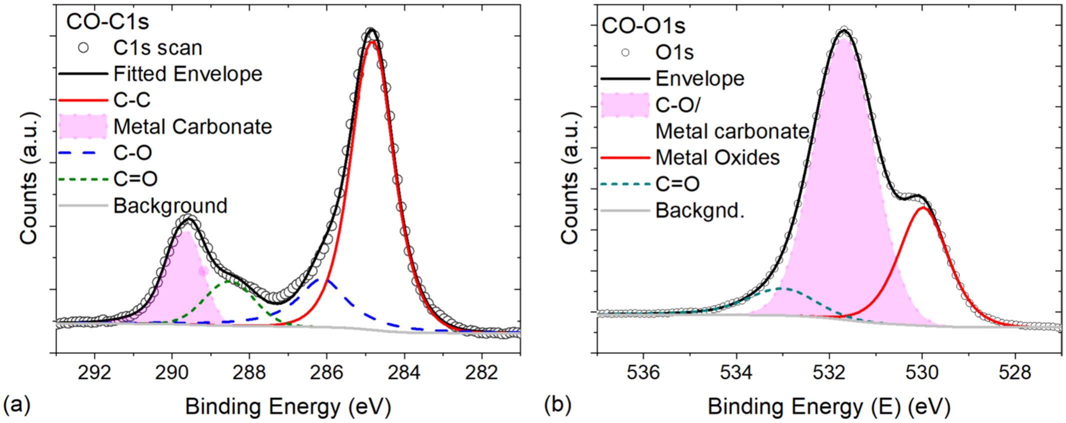


Fig. 14 **a** C1s and **b** O1s spectra from track rubbed in CO

the inert gases, suggesting negligible tribofilm formation, except for a possible slight reduction in friction for ethane towards end of test. Propane apparently forms a tribofilm slowly, such that friction drops to a relatively low value partway through each test, and this is reflected in an intermediate wear result. The two butanes show very low friction after 1–5 min rubbing and low wear, suggesting quite rapid tribofilm formation. There is no apparent difference in performance between the linear and the branched butane.

Previous work using both gaseous and liquid saturated hydrocarbons has shown that these can form lubricious carbonaceous films readily during rubbing in oxygen-free atmospheres [23, 39, 40]. It is generally accepted that this film formation is driven by the severe conditions present in rubbing contacts that break C–C and/or C–H covalent bonds to form free radical species that then rearrange, lose hydrogen atoms, and combine to form graphitic material on the rubbing surfaces. There is some debate about the relative importance of the impact of mechanical stresses and surface catalysis on the reaction, and it is probable that catalysis is most important with surfaces that contain catalytically-active atoms such as Cu, Ni and Pt, but that mechanochemical effects are more prevalent with bearing steels. Previous work has shown that propane forms a low friction carbonaceous film on rubbing AISI 52100 surfaces [23] and that butane reacts on rubbing ceramic surfaces to form a high molecular weight material [26]. The formation of such films by methane or ethane on steel surfaces has not been reported but has been shown that methane will form such films on highly catalytic nickel-containing surfaces [22]. The fact that methane does not appear to form effective tribofilms on steel surfaces but does so on catalytic ones may imply that its reaction is controlled by a catalytic rather than mechanical response. Two effects might explain the fact that carbonaceous tribofilm formation by saturated hydrocarbons increases with molecular weight. One is simply that there should be stronger adsorption of the gaseous molecules on the surfaces as the molecular weight increases. The second is that the mechanical forces experienced by interior C–C bonds will increase with the size of the groups attached to each C atom as forces are transmitted along the chain. Also, of course, methane, with just one carbon atom, cannot experience C–C bond cleavage to form a hydrocarbyl free radical.

To confirm the formation of a carbonaceous tribofilm, an HPR disc from a test with n-butane was analysed using Raman spectroscopy as shown in Fig. 15. Characteristic carbon D- and G- bands can be seen in spectra from some parts of the worn surface, while only iron oxide peaks are observed in other places. The morphology of the tribofilm shown by optical micrographs confirmed that the tribofilm is heterogeneous. It should be noted that the iron oxide may have been formed after tests, when samples were exposed briefly to air for Raman analysis.

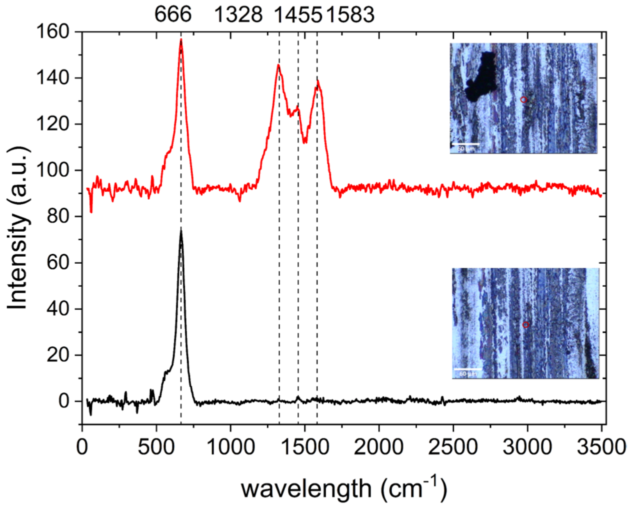


Fig. 15 Raman spectra from HPR disc track rubbed in n-butane

5.5 Unsaturated Hydrocarbons

Figures 6 and 7 showed that ethene, propene and ethyne give very low friction and wear, implying that they form protective tribofilms very readily. It is well known that unsaturated hydrocarbons form carbonaceous films more easily that saturated ones [37, 41]. The precise mechanism of formation is not yet clear—it is evidently promoted by rubbing, but the extent to which simple polymerisation as opposed to stress-driven radical reactions occurs in not known.

Raman spectra from various regions of disc surfaces rubbed in ethene and ethyne are presented in Fig. 16. Compared to results from butane, the surface coverage of carbonaceous materials increases as we go from this to ethene, then to ethyne. This supports the interpretation that the ease of carbonaceous film formation increases with the degree of unsaturation of the gas.

Although the formation of carbonaceous film increases with unsaturation, this does not result in a progressive reduction in friction and wear; wear is similar for all three unsaturated hydrocarbons studied while friction is actually slightly higher for ethyne than for ethene.

The differences in tribological performance between various hydrocarbon molecules may also stem from their difference in adsorption behaviour at the test conditions. Research on vapour phase lubrication with alcohol has shown that the concentration of adsorbed molecules is linked directly to partial pressure and can correlate with a reduction in surface adhesion [42]. Using information available from the NIST Chemistry WebBook [43], the saturation pressures of ethene and propane at 25 °C were estimated using the Antoine Equation to be about 60 bar and 10 bar respectively. This means that, based on the proximity of its partial pressure to saturation pressure, propane should have been more

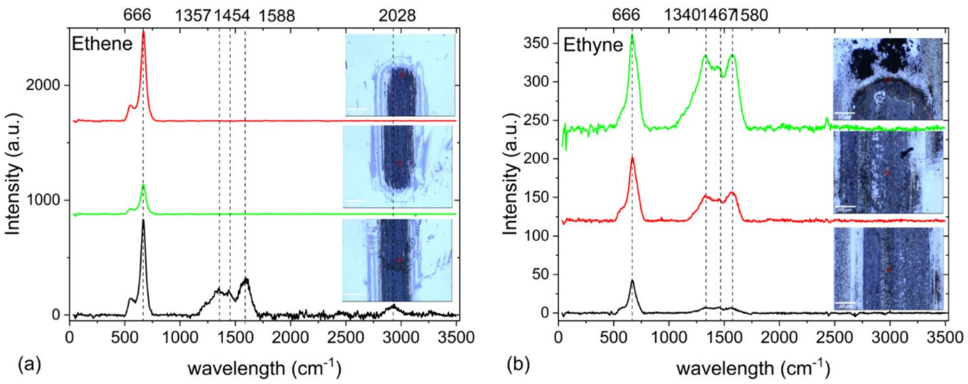


Fig. 16 Raman spectra of disc surfaces rubbed in **a** ethene and **b** ethyne

readily adsorbed on rubbing surfaces than ethene; implying that it might give lower friction than ethene. This, however, contradicts our results and thus lends support to the low friction of unsaturated hydrocarbons observed in this work being due to its higher reactivity.

6 Conclusions

This study has used a sealed, reciprocating, ball of flat tribometer, the HPR, to measure the friction and wear properties a steel/steel sliding contact in a range of gaseous environments of tribological interest. It is found that the inert gases helium and argon and also nitrogen and hydrogen give high friction and wear indicating that they form little or no protective tribofilm. Dry air and pure oxygen give friction similar to nitrogen but produce extremely high wear. This is believed to originate from oxidational wear when rapidly-forming iron oxide is abraded from the rubbing surfaces.

Ammonia and carbon monoxide both show relatively low friction and wear, indicating that they form tribofilms on the rubbing surfaces. Gas-switching studies suggest that these tribofilms are initially weak but then they become stronger and have lower friction after repeated switching. XPS analysis on the rubbed surfaces shows that ammonia both adsorbs on the surfaces and forms nitrides, while carbon monoxide forms a carbonate.

The saturated hydrocarbon gases show decreasing friction and wear with increase of molecular weight. Thus methane and ethane show no friction reduction, propane forms a film only after about 30 min of rubbing and n-butane and isobutane form films after between 1 and 5 min of rubbing. Raman analysis of the tribofilm formed on a disc track rubbed in n-butane shows the presence of D- and G- carbon bands, characteristic of graphitic carbon.

The unsaturated gases, ethene, propene and ethyne all show an immediate reduction in friction and give low wear. Raman analysis of the rubbed surfaces shows the formation of a carbonaceous film which increases with the level of unsaturation of the hydrocarbon.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11249-024-01911-y.

Acknowledgements The authors wish to thank PCS Instruments for supply of an HPR test rig, the Shell-Imperial College University Technology Center for Mobility and Lubricants for support for Jie Zhang, and Shouyi Yin for the help with XPS.

Author Contributions JZ: Investigation, Analysis; JSSW: analysis, writing—review and editing; HAS: conceptualisation, supervision, project administration, writing.

Funding The authors have not disclosed any funding.

Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing interests The authors declare no competing interests.

References

1. Bowden, F.P., Hughes, T.P.: The friction of clean metals and the influence of adsorbed gases. The temperature coefficient of friction. Proc. Roy. Soc. Lond. **A172**, 263–279 (1939)
2. Soda, N., Sasada, T.: Mechanism of lubrication by surrounding gas molecules in adhesive wear. Trans. ASME J. Lub. Tech. **100**, 492–497 (1978)
3. Mishina, H.: Atmospheric characteristics in friction and wear of metals. Wear **152**, 99–110 (1992)
4. Mishina, H.: Chemisorption of diatomic gas molecules and atmospheric characteristics in adhesive wear and friction of metals. Wear **180**, 1–7 (1995)

5. Wilson, J.E., Stott, F.H., Wood, G.C.: The development of wear-protective oxides and their influence on sliding friction. Proc. Roy. Soc. Lond. **A369**, 557–574 (1980)
6. Zhang, Q.Y., Chen, K.M., Wang, L., Cui, X.H., Wang, S.Q.: Characteristics of oxidative wear and oxidative mild wear. Tribol. Intern. **61**, 214–223 (2013)
7. Wu, X., Cong, P., Nanao, H., Minami, I., Mori, S.: Tribological behaviors of 52100 steel in carbon dioxide atmosphere. Tribol. Lett.. Lett. **17**, 925–930 (2004)
8. Nunez, E.E., Polychronopoulou, K., Polycarpou, A.A.: Lubricity effect of carbon dioxide used as an environmentally friendly refrigerant in air-conditioning and refrigeration compressors. Wear **270**, 46–56 (2010)
9. Rosenberg, S.J., Jordan, L.: Influence of oxide films on the wear of steels. J. Res. Natl. Bur. Stan. **13**, 267–279 (1934)
10. Buckley, D.H., Johnson, R.L.: Effect of Inert, Reducing and Oxidising Atmospheres on Friction and Wear of Metals to 1000°F. NASA, Washington (1961)
11. Batchelor, A.W., Stachowiak, G.W., Cameron, A.: The relationship between oxide films and the wear of steels. Wear **113**, 203–223 (1986)
12. Fink, M.: Wear oxidation—a new component of wear. Trans. Am. Soc. Steel Treat. **18**, 1026–1034 (1930)
13. Smith, A.F.: Influence of environment on the unlubricated wear of 316 stainless steel at room temperature. Tribol. Intern. **19**, 3–10 (1986)
14. Feng, I.M., Uhlig, H.H.: Fretting corrosion of mild steel in air and in nitrogen. Trans. ASME J. Appl. Mech. **21**, 395–400 (1954)
15. So, H.: The mechanism of oxidational wear. Wear **184**, 161–167 (1995)
16. Cornelius, D.E., Roberts, W.H.: Friction and wear of metals in gases up to 600 C. ASLE Trans. **4**, 20–32 (1961)
17. Velkavrh, I., Ausserer, F., Klien, S., Brenner, J., Forêt, P., Diem, A.: The effect of gaseous atmospheres on friction and wear of steel–steel contacts. Tribol. Intern. **79**, 99–110 (2014)
18. Zhang, Y., Jourani, A.: Combined effect of microstructure and gaseous environments on oxidative and adhesive wear of dual-phase steel. J. Mater. Eng. Perf. **30**, 9333–9351 (2021)
19. Kruger, J., Yolken, H.T.: Room temperature oxidation of iron at low pressures. Corrosion **20**, 29t–33t (1964)
20. Velkavrh, I., Ausserer, F., Klien, S., Voyer, J., Ristow, A., Brenner, J., Forêt, P., Diem, A.: The influence of temperature on friction and wear of unlubricated steel/steel contacts in different gaseous atmospheres. Tribol. Intern. **98**, 155–171 (2016)
21. Murray, S.F., Johnson, R.L., Swikert, M.A.: Boundary Lubrication of Steel with Fluorine- and Chlorine-Substituted Methane and Ethane Gases. NACA, Ohio (1955)
22. Ramirez, G., Eryilmaz, O.L., Fatti, G., Righi, M.C., Wen, J., Erdemir, E.: Tribochemical conversion of methane to graphene and other carbon nanostructures: implications for friction and wear. ACS Appl. Nano Mater. **3**, 8060–8067 (2020)
23. Zhang, J., Bolle, B., Wong, J.S.S., Spikes, H.A.: Influence of atmosphere on carbonaceous film formation in rubbing, metallic contacts. Tribol. Lett.. Lett. **72**, 4 (2024)
24. Lauer, J.L., Dwyer, S.R.: Tribochemical lubrication of ceramics by carbonaceous vapors. Tribol. Trans.. Trans. **34**, 521–528 (1991)
25. Blanchet, T.A., Lauer, J.L., Liew, Y.F., Rhee, S.J., Sawyer, W.G.: Solid lubrication by decomposition of carbon monoxide and other gases. Surface Coatings Tech. **68**, 446–452 (1994)
26. Nakayama, K., Hashimoto, H.: Triboemission, tribochemical reaction, and friction and wear in ceramics under various n-butane gas pressures. Tribol. Intern. **29**, 385–393 (1996)
27. Greenwood, J.A.: An interpolation formula for flash temperatures. Wear **150**, 153–158 (1991)
28. Reddyhoff, T., Schmidt, A., Spikes, H.A.: Thermal conductivity and flash temperature. Tribol. Lett.. Lett. **67**, 22 (2019)
29. Li, Y.S., Jang, S., Khan, A.M., Martin, T.V., Ogrinc, A.L., Wang, Q.J., Martini, A., Chung, Y.W., Kim, S.H.: Possible origin of D-and G-band features in Raman spectra of tribofilms. Tribol. Lett.. Lett. **71**, 57 (2023)
30. Fouvry, S., Kapsa, P., Vincent, L.: Quantification of fretting damage. Wear **200**, 186–205 (1996)
31. Quinn, T.F.J.: Role of oxidation in the mild wear of steel. Br. J. Appl. Phys. **13**, 33–37 (1962)
32. Quinn, T.F.J.: Oxidational wear. Wear **18**, 413–419 (1971)
33. Quinn, T.F.J.: Review of oxidational wear: Part I: the origins of oxidational wear. Tribol. Intern. **16**, 257–271 (1983)
34. Quinn, T.F.J.: Review of oxidational wear part II: recent developments and future trends in oxidational wear research. Tribol. Intern. **16**, 305–315 (1983)
35. Vinod, K.R., Saravanan, P., Sakar, M., Balakumar, S.: Insights into the nitridation of zero-valent iron nanoparticles for the facile synthesis of iron nitride nanoparticles. RSC Adv. **6**(51), 45850–45857 (2016)
36. Peng, H., Mo, Z., Liao, S., Liang, H., Yang, L., Luo, F., Song, H., Zhong, Y., Zhang, B.: High performance Fe-and N-doped carbon catalyst with graphene structure for oxygen reduction. Sci. Rep. **3**(1), 1765 (2013)
37. Wojciechowski, P., Lewandowski, M.: Iron nitride thin films: growth, structure, and properties. Cryst. Growth Des.. Growth Des. **22**, 4618–4639 (2022)
38. Lukashuk, L., Yigit, N., Rameshan, R., Kolar, E., Teschner, D., Hävecker, M., Knop-Gericke, A., Schlögl, R., Föttinger, K., Rupprechter, G.: Operando insights into CO oxidation on cobalt oxide catalysts by NAP-XPS, FTIR, and XRD. ACS Catal.Catal. **8**(9), 8630–8641 (2018)
39. Zhang, J., Campen, S., Wong, J., Spikes, H.: Oxidational wear in lubricated contacts—or is it? Tribol. Intern. **165**, 107287 (2022)
40. Li, Y.S., Jang, S., Bhuiyan, F.H., Martini, A., Kim, S.H.: Molecular structure and environment dependence of shear-driven chemical reactions: tribopolymerization of methylcyclopentane, cyclohexane and cyclohexene on stainless steel. Tribol. Lett.. Lett. **71**, 49 (2023)
41. He, X., Kim, S.H.: Mechanochemistry of physisorbed molecules at tribological interfaces: molecular structure dependence of tribochemical polymerization. Langmuir **33**, 2717–2724 (2017)
42. Kim, S.H., Dugger, M.T., Erdemir, A., Barnette, A.L., Hsiao, E., Marino, M.J., Eryilmaz, O.: MEMS lubrication with alcohol vapour. Tribol. Mater. Surfaces Interfaces **4**(3), 109–114 (2010)
43. Linstrom, P.J., Mallard, W.G.: The NIST chemistry WebBook: a chemical data resource on the internet. J. Chem. Eng. Data **46**(5), 1059–1063 (2001)