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Full Length Article

An investigation of the effect of temperature on the oxidation processes of metallic diesel engine fuel system materials and B100 biodiesel from used cooking oil in exposure testing

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A B S T R A C T

Biodiesel is increasingly being used in automotive and other engine applications because of its potential to contribute to the reduction of CO\(_2\) and other harmful emissions. However, biodiesel is known to be more corrosive in contact with metallic components than petroleum diesel. This work explores the corrosion of aluminium, steel, brass and copper metallic coupons exposed to B100 biodiesel at 25, 80, 90, 100, 110 and 120 °C. The metals that were chosen are commonly found in automotive engines. The B100 in each experiment was sampled at 48, 100, 150, 200 and 270 h and examined by GCMS to determine compositional changes. It was found that corrosion rates for copper were 10x faster than brass and approximately 100x faster than for mild steel, Al7075 and Al1050. Activation energies for corrosion were calculated from mass loss and ICP, with good correlation between the two methods for Cu containing samples. By mass loss, the activation energies for Cu, Brass, Al7075 and Al1050 were calculated to be −47.9 kJ mol\(^{-1}\), −85.4 kJ mol\(^{-1}\), −86.7 kJ mol\(^{-1}\) and −54.4 kJ mol\(^{-1}\), respectively. By ICP analysis, the activation energies for Cu, Brass, and Al7075 were calculated to be −57.9 kJ mol\(^{-1}\), −90 kJ mol\(^{-1}\) and −140 kJ mol\(^{-1}\), respectively. Corrosion rates in brass and copper samples were faster owing to the direct reaction of copper with the fatty acid. The copper was found to cause chain scission and greater degradation of the biodiesel.

1. Introduction

The International Energy Agency (IEA) has predicted that global CO\(_2\) emissions are expected to decline by 8%, or almost 2.6 gigatonnes (Gt) as a result of the 2020 SARS-CoV-2 global health crisis [1]. In particular, diesel demand has fallen by 1.5 million barrels per day (mb/d) due to lower economic activity and restrictions to rail and bus transport and is expected to remain lower by 7% until the end of 2020 (2mb/d) [1]. However, diesel fuel continues to be the main fuel for the majority of heavy-duty vehicles such as ships and trucks as well as in countless agricultural and industrial vehicles. The efficiency and durability of diesel engines have made them the ideal power plants for these vehicles. There is therefore an ongoing need to address the way in which emissions from these types of engines can be decreased to address the need to globally reduce temperature changes owing to climate change for the future sustainability of the planet. Biodiesel is thus increasingly being used as a means of reducing CO\(_2\) emissions from the vehicle fleet with the EU, the USA and the UK setting targets for the use of biodiesel blends of 10 (by 2020), 25 (2022) and 12.4% (by 2032) respectively.

King [2] noted that biofuels offer potential advantages over conventional fuels for the medium term, as biofuels have the potential to work with existing diesel engine technology and they can be introduced as blends to conventional diesel fuel. Biofuels reduce the overall carbon dioxide generated and are said to decarbonize the fuel, either through fuel switching and/or by reducing the amount of CO\(_2\) involved in the production of fuels. Thus, using biofuels can result in reduced greenhouse gas emissions compared to fossil fuels [3–6]. Future vehicle technologies may develop solutions for decreasing emissions that rely on alternative fuels, such as hydrogen, and because of this, electric vehicles will become increasingly prevalent. In the medium term however, liquid hydrocarbons will continue to be used for transport applications [5,7]. Pereira [8] compared the use of B100 with diesel on a fleet of buses over an 18 month period. The lubricating oil was monitored for Al, Pb, Fe and Cu content and showed that Al, Pb and Fe engine components showed decreased wear due to increased lubricity.
of B100 over diesel but increased wear of Cu components due to increased reactivity Cu with B100 over diesel. The decreased viscosity of the lubricating oil with time led to reduced service times for B100 buses to ~⅔ that of diesel buses. In addition to the use of biofuels, water-blended diesel emulsions have shown potential to improve engine performance and also reduce levels of particulate matter (PM) and nitrogen oxide emissions (NOx) from diesel engines [9–12] and gives an alternative approach for future vehicles with lower emissions.

Biodiesels are fatty acid alkyl esters that are derived from a range of different sources, such as palm, canola, corn, rapeseed and sunflower oils. The advantage of biodiesel is that it is close in fuel properties such as flash point, fire point, calorific value, viscosity, density and cetane

| Time/minutes | Nomenclature | Formula      | Name                                           | Relative fraction/% |
|--------------|--------------|--------------|------------------------------------------------|---------------------|
| 20.30        | 16.0         | C₁₇H₃₄O₂     | Hexadecanoic acid methyl ester                  | 4                   |
| 21.97        | 18.2         | C₁₉H₃₄O₂     | 9,12 Octadecenoic acid (Z,Z) methyl ester       | 29                  |
| 22.03        | 18.1         | C₁₉H₃₆O₂     | 9 Octadecenoic acid (Z) methyl ester            | 66                  |
| 22.06        | 18.0         | C₁₉H₃₈O₂     | Octadecanoic acid methyl ester                  | 1                   |

Fig. 1. Composite image showing photographs of all experiments after 270 h.
number to petroleum diesel. In some literature it has been shown to reduce both CO₂ and NOₓ emissions [9,13] whilst maintaining or improving engine performance [14–16]. There are also challenges in the use of biodiesel in that it can lead to increased corrosion and oxidation of metallic engine components [17–20] including fuel injection systems [21]. Additionally, biodiesel can have problems at low temperatures, where it can gel, although this can be avoided by the use of appropriate anti-gelling agents [22]. Chandran [23], Fazal et al [24] and Zuleta et al [25] have provided comprehensive critical reviews of the way in which biodiesel interacts with diesel engine materials and showed that the proportion of biodiesel in the blend, the total acid number (TAN) and presence of water all affect biodiesel oxidation. Another challenge with biodiesel is that it oxidises more rapidly than conventional diesel. The oxidation reactions transform the esters in biodiesel to alcohols, ketones, ethers, alkanes, organic acids, aldehydes and oligomers. The different reaction pathways are described in detail by Zuleta et al and Bannister et al [26,27]. The oxidation reactions result in increased viscosity of the fuel and degraded performance. The oxidation rates are affected by a range of factors, including the chemistry of the biodiesel itself, the temperature and the metallic components in the fuel system (as well as the way in which fuels are stored and transported before use in the engine) [28–31].

In an automotive engine, fuel comes into contact with many different components. Biodiesel is known to cause enhanced corrosion due to the water and free fatty acids contained within the fuel [18,20]. Copper components in particular are known to suffer enhanced corrosion in biodiesel [19]. The purpose of the current work is to provide data on rate of reaction of common metals and alloys with B100 diesel.
Fig. 4. (a) GC–MS traces for Blank and Cu samples at 25 °C and 120 °C after 270 h, 5% dilution, showing main components. (b) GC–MS traces for Blank and Cu samples at 25 °C and 120 °C after 270 h, 5% dilution, showing close up of 3–20 min region. (c) GC–MS traces for Blank and Cu samples at 25 °C and 120 °C after 270 h, 5% dilution, showing close up of 20.4–21.9 min region. (d) GC–MS traces for Blank and Cu samples at 25 °C and 120 °C after 270 h, 5% dilution, showing close up of 23–26 min region.
and explore the mechanisms involved in the onset of the corrosion process for samples fully submerged in B100. Furthermore, the fully submerged position of specimens in biodiesel was designed to simulate the exposure of components within an engine exposed to biodiesel for extended periods at different temperatures.

In this work we have focused on looking at the way in which corrosion initiates and the corrosion rate for a number of different metal alloys across a wide range of temperatures. Other studies have looked predominantly at biodiesel and biodiesel blends produced straight from crops and by comparison the B100 biofuel we have used was based on recycled used cooking oils. In addition, we have investigated the link between the metallic alloy corrosion and the details of the oxidation mechanism of the fuel.

2. Experimental methods and materials

Corrosion characterisation tests were carried out on metal coupons of copper, brass, aluminium Al1050 alloy, aluminium Al7075 alloy and steel when in contact with biodiesel B100 at 25 °C, 80 °C, 90 °C, 100 °C, 110 °C and 120 °C for 270 h. During the tests, fuel temperature was maintained and monitored. The samples used for the tests were brass Cu30Zn (51 mm X 30 mm X 1.6 mm), copper (51 mm X 25 mm X 2 mm) with the composition of 100% Cu, mild steel (50 mm X 30 mm X 2 mm) with the composition of 0.1% C, Al1050 alloy (51 mm X 20 mm X 1.5 mm) with the composition of 99.5% Al and Al7075 (51 mm X 20 mm X 1.5 mm) with the composition of Al, Mg, Cu and Zn. One 5 mm diameter hole was drilled at the corner of each metal sample and nylon fishing line used for hanging the samples in the fuels, so that they were not in contact with the walls of the vessel. Before starting the immersion corrosion tests, all metallic samples were prepared using the process outlined below:

All samples were prepared in accordance with ASTM G31 [32] by wet grinding with silicon carbide abrasive papers (400 to 1200 grade) and then polishing to a 6 µm diamond finish on all faces and edges. The samples were then washed with water and methanol and then ultrasonically cleaned in acetone for 20 min before being dried by a heater. The samples were dried to constant weight.

Table 2
Assignment of peaks present in GC/MS.

| Peak 0–20 time/min | Present for | Assignment |
|--------------------|-------------|------------|
| 10.34              | blank, Al1, Al7, Fe, brass, Cu 120 °C | Octanoic acid methyl ester |
| 13.26              | brass, Cu 120 °C | unidentified |
| 13.45              | brass, Cu 120 °C | unidentified |
| 14.80              | blank, Al1, Al7, Fe, brass, Cu 120 °C | Oxan-nonanoic acid |
| 15.94              | blank 25 °C | unidentified |
| 16.80              | blank, Al1, Al7, Fe, brass, Cu 120 °C | unidentified |
| 17.97              | blank, Al1, Al7, Fe, brass, Cu 120 °C | unidentified |
| 18.20              | All | C14,0. Methyl tetradecanoate C13H26O2 |
| 20.08              | All | unidentified |
| 20.12              | All | 16.1, Hexadecanoic acid methyl ester C16H34O2 |
| 20.21              | All | unidentified |
| 20.32              | All | 16.0, Hexadecanoic acid methyl ester C17H36O2 |
| 20–22 min Fig. 4.b |                |            |
| 20.46              | All | unidentified |
| 20.78              | All | unidentified |
| 21.08              | All | unidentified |
| 21.28              | All | unidentified |
| 21.291             | All | 18.2 |
| 21.971             | All | 18.1 |
| 22.25              | All | 18.0 |
| 22–26 min, Fig. 4.d |                |            |
| 22.79              | All | unidentified |
| 23.43              | All except blank 25 °C | unidentified |
| 23.61              | All | C17H32O3 methyl 9,10 epoxyoctadecanoate |
| 23.78              | All | C17H34O3 cu-11-eicosanoic acid methyl ester |
| 23.82              | All | C17H34O3 methyl 13, 16, docosadienoate |
| 23.97              | All | C17H36O3 eicosanoic acid methyl ester |
| 23.987 * shoulder  | (All Al7, Fe, blank) 120. Not 25 °C, not Cu, brass | C17H34O3 Octadecanoic acid 9, 10 dihydroxy methyl ester |
| 24.26              | All except blank 25 °C | unidentified |
| 24.50              | All except blank 25 °C | C18H34O3 methyl 5, 9, octadecadienoate |
| 24.95              | All except blank 25 °C | C18H34O3 Methyl cis 6, trans 8, cis 12 octadecatrienoate |
| 25.02              | All except blank 25 °C | C18H34O3 8 (5 hexyl, -2-furyl) octanoate |
| 25.42              | All | C18H34O2 methyl 2 octylcyclopropene 1- ocanoate |
| 25.59              | All | C18H34O2 Docosanoic acid methyl ester |
| 25.62              | All | C18H34O2 Docosanoic acid methyl ester |

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Fig. 5. Corrosion rates by mass loss (red circle) and ICP measurement (black square) for Al1050, Al7075, Steel Brass and Copper samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
washed with detergent and water with light brushing using a soft nylon bristled brush and then rinsing with methanol and then acetone to remove the testing fuels from the surfaces and dried in hot air. To avoid damaging any potentially corroded surfaces, the samples were not subjected to ultrasonic cleaning. The samples were repeatedly cleaned and dried to constant weight in accordance with ASTM G1 [33].

Before and after the immersion corrosion tests, all metal samples were weighed by an electronic balance accurate to 0.0001 g. One sample from each metal was used at 25 °C, 80 °C, 90 °C, 100 °C, 110 °C and 120 °C. The weight loss for each sample was recorded. This allowed the corrosion behaviour of the metal samples when in contact with biodiesel and diesel fuel to be observed through measurement of their corrosion rates and studying the morphology surface changes for them. The average weight loss for each sample was converted to corrosion rate by using the equation [32]:

\[
\text{Corrosion Rate (mm year}^{-1}) = \frac{W}{\rho At}
\]

where: Corrosion rate is calculated in mm year\(^{-1}\), \(W\) = weight loss in grammes, either by weight loss of the coupon or calculated from the concentration of metal in solution, \(\rho\) = density in g cm\(^{-3}\), \(A\) = surface area in contact of fuels in mm\(^2\) and \(t\) = test duration in years.

Fuel samples were analysed before and during corrosion immersion tests by Gas Chromatography Mass Spectroscopy (GCMS) (Perkin Elmer TurboMass GCMS, Perkin Elmer Seer Green, UK) in the chemistry department at the University of Leicester. Samples of 2 ml were removed by pipette. GCMS was performed on dilutions of 5 vol% and 0.5 vol% in carbon tetrachloride using 0.1 ml aliquots. Both fuel compositional changes and the presence of metal species were investigated to an accuracy of ± 0.5 ppm by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on an Agilent 5110 (Stockport, UK). Fuel samples were sent to Oil Check Laboratory Ltd (Doncaster, UK) for this analysis and each sample was analysed 3 times. Each sample consisted of 0.5 ml of fuel diluted in 4.5 ml kerosene containing 10 ppm Co as standard.

The B100 biodiesel used in these experiments was processed from Used Cooking Oils (UCO) and purchased from Biofuel Refineries Ltd (High Wycombe, UK). It had a density of 0.881 g cm\(^{-3}\), a viscosity of 3.1 cSt at 40 °C and a Total Acid Number (TAN) of 0.23 mg KOH g\(^{-1}\). The Oxidation Stability of the B100 was not supplied and is unavailable, however fuels of similar origin and composition typically show a range from 1.2 to 9 h at 110 °C [25].

The unreacted biodiesel was analysed by GCMS and consisted of four main Fatty Acid Methyl Ester (FAME) components. These were identified using the NIST database software as 16.0, 18.2, 18.1 and 18.0 methyl esters as shown in Table 1. The relative quantities of these constituents were calculated for B100 from relative chromatogram areas, as is standard practice for GCMS.

The physical and chemical behaviour of the alloys before and after immersion tests were characterised by optical microscope (Olympus GX53, Southend-on-Sea, UK) and SEM (Sirion 200 FEGSEM (FEI, Eindhoven, Netherlands)) with Princeton Gamma Technology Spirit EDX.

The colour change of the fuel was also noted. Each glass jar contained one specimen of the alloys samples and each specimen was removed for visual inspection and surface analysis after 270 h. Temperatures were controlled using a thermocouple and hot plate stirrer. The thermocouple was isolated from the biodiesel by a glass sheath.

### 3. Results and discussion

The exposure experiments showed a range of related behaviours across the different metals and temperatures studied. The most obvious change is in the colour of the B100 as shown in Fig. 1. It is clear that elevated temperature has an effect, with the B100 turning from a pale yellow colour towards brown at 120 °C for the blank control.

### Table 3

| Method   | \(E_a/\text{kJ mol}^{-1}\) |
|----------|--------------------------|
| Cu-ICP   | –57.9                    |
| Cu-mass  | –47.9                    |
| brass-ICP| –87.2                    |
| brass-mass| –85.4                  |
| Al7075-ICP| –140                    |
| Al7075-mass| –90                     |
| Al1050-mass| –54.4                  |

Fig. 6. Arrhenius plots for Al1050, Al7075, Steel Brass and Copper samples.
experiment. There might be a slight darkening at 110 °C. The Al1050 and Al7075 samples showed similar colour changes to the blank samples. With mild steel, the colour change was more pronounced and the change at 110 and 120 °C is clearly observable. With brass, and more so with Cu coupons, the colour change is dramatic and observable at all temperatures. It is notable that the B100 appeared to darken slightly at 25 °C for all samples, including the control.

GCMS measurements were performed for all exposure tests periodically throughout the experiments. The B100 consists of four main components and these are shown outlined in bold in Table 1. They are identified confidently as methyl esters of 16.0, 18.2, 18.1 and 18.0. There are other minor constituents at < 1% of total composition, which are of similar chemistry to the main constituents, but varying only in the number of carbon atoms in the chain. They can be assumed to behave in a similar fashion to the main constituents but are in such low concentration that any reaction products were unobservable. Fig. 2 plots the relative concentration of the four main components of B100 measured at different times throughout the exposure test. At 25 °C, with no metal coupon present, the relative concentration of all components remains constant. Close examination of GCMS results at high concentration showed no sign of any products of chemical reaction to this sample. At elevated temperatures, the relative concentrations of the four main components change with time.

The plot for the blank B100 sample at 120 °C in Fig. 2 shows that the
amount of 18.2 decreases relative to other constituents from ~30% to ~20% after 270 h. There is a commensurate rise in the amount of 18.1.

In the presence of Cu at 25 °C and 120 °C a similar effect is observed, with loss of 18.2 to ~20% at 25 °C and to < 20% at 120 °C. All other samples showed similar behaviour. Blank, Al1050, Al7075 and mild steel all showed no change in concentration at 25 °C, but all other experiments showed some loss of 18.2 relative to other constituents with time. Of these, Cu at 120 °C showed the greatest loss of 18.2, hence its relevance in Fig. 2d, where it acts as a demonstration of extreme behaviour.

Fig. 3 plots GCMS traces for blank 25 °C, blank 120 °C, Cu 25 °C and Cu 120 °C at 0.5% dilution. There are no other peaks of any significance visible in these traces. In order to observe the products of chemical reactions taking place, it was necessary to repeat the GCMS at a more concentrated dilution of 5%. Fig. 4a shows GCMS traces for the same four samples at 5% concentration.

Fig. 4a-j shows GCMS for various samples at 5% concentration. The products of the chemical reactions of the four main components were found to be present in low concentrations and hence these are best observed and identified by performing GCMS on more concentrated solutions at 5%.

These solutions are too concentrated for analysing the main components, which are not separated properly, as seen in Fig. 4a at 22.15 min. Table 2 shows the position and assignment of all peaks observed in the exposure experiments. The reaction products were observed to fall into two main categories: reaction products due to chain scission reactions and reaction to oxidation processes occurring at unsaturated bonds in the hydrocarbon chain. These reactions occur naturally for B100 samples at 80–120 °C, showing the inherent oxidative instability of this fuel. According to Neff, et al [34], 18.2 is 50 times more oxidisable than 18.1, hence it is reasonable to concentrate purely on 18.2 as the primary reactant in all processes hereafter.

Products formed by chain scission are lighter than the starting materials and will exit the column more rapidly. Products of chain scission reactions are given in Table 2 in the 3–20 min region, which is seen in close up in Fig. 4b. It is notable that the peaks at 10.34 and 14.80 min Cu (also observed with brass) are considerably increased in intensity and these have been assigned as octanoic acid methyl ester and oxanonoic acid respectively, produced by oxidative chain scission at the C–C double bonds. Hence, chain scission reactions incorporating oxidation are considerably accelerated in the presence of Cu and brass compared to other metals studied. The peaks in this region are in very low concentration and are very difficult to identify confidently using the GCMS NIST software package. From 20 to 22 min, all
samples except blank, Al1050 and Al7075 showed a similar pattern of behavior, with increased peak height at 20.77 min and decreased peak height at 21.06 min compared to unreacted B100. Fig. 4c shows the change in relative peak heights for Cu and blank samples at 120 °C and 270 h compared to the Cu and blank samples at 25 °C. These peaks proved impossible to identify, as they are only present in very low concentrations in all cases making identification challenging.

The highest concentrations of reaction products are observable between 23 and 26 min. In this region, all reacting samples show a similar pattern of peaks with few exceptions. This behaviour is clear in Fig. 4a at 5% dilution for the Cu sample at 25 °C and the blank and Cu samples at 120 °C and 270 h.

These are compared against the blank 25 °C control, which does not show any of these extra peaks. The 23–26 min region is examined more closely in Fig. 4d. The peaks are tentatively assigned using NIST software in Table 2. The 23–26 min region shows the most changes for all samples examined by GCMS and the concentration of these extra peaks is seen to increase in intensity with increasing temperature for all experimental conditions. Blank, Al1050, Al7075 and mild steel do not show these peaks in the 23–26 min region at 25 °C, and only show trace starting materials identified as methyl esters of: 20.1 at 23.79 min, 20.0 at 23.98 min, 22.1 at 25.42 min and 22.0 at 25.6 min. For all other sample/temperature combinations, there are a series of peaks which are difficult to assign due to their low concentrations. However, wherever
peaks can be identified, they are all seen to be oxidation products of double bonds. Given that 18.2 is the most reactive species present by a significant margin, it is likely that these are all products of oxidation processes occurring to 18.2. Bouaid and Martinez [35] showed the propensity for 18.2 to undergo oxidation type reactions via an auto oxidative reaction initiated by a radical process removing the H at the bis-allylic position. Once this position has been radicalized, it reacts readily with oxygen and forms peroxide. From this point a range of reaction pathways are possible producing a range of products seen in the 23–26 min region which are all conceivable as products of radical oxidation at the bis-allyl position.

It is notable that for blank, Al1050 and Al7075 experiments at any given temperature, the relative concentrations of oxidative products all show similar relative concentrations, indicating that the metal coupon plays little part in the reactions. With mild steel however, there is a decrease in the peak area of the shoulder at ~24 min ascribed to octadecanoic acid 9, 10 dihydroxy methyl ester, and an increase in the area of the doublet observed at 24.95–25.02 min assigned as furyl and cyclopropenyl groups.

The change in colour of the B100 is coincident with the increased mass loss, ICP analysis and GCMS results observed after 270 h.

Corrosion rates calculated from mass loss and ICP data are presented in Fig. 5. The corrosion rate calculated by mass loss and ICP for brass undergoes a notable increase beginning at 100 °C, as seen in Fig. 5. For both Al1050 and Al7075, the ICP showed no AI in B100 solution. However, mass loss indicated a small amount of material loss at elevated temperatures. This discrepancy may be explained by insolubility of reaction products and hence they are not observed in ICP. Mass loss for steel was not measured and the ICP showed no Fe in solution with concentrations similar to those observed for Al.

The corrosion rates determined at different temperatures were compared to those obtained by other researchers under appropriate conditions. Hu et al [36] obtained a corrosion rate of 0.023 mm yr−1 for Cu exposed to biodiesel at 43 °C for 60 days, and 0.018 mm yr−1 and 0.003 mm yr−1 for mild steel and Al respectively. This is considerably higher than our observed results. However, a reason for this may be found in the work of Fazal et al [19] who exposed palm diesel to Cu and mild steel at RT for 20, 40 and 60 days. The corrosion rate after 20 days was 0.0115 mm yr−1 for Cu and 0.0013 mm yr−1 for mild steel. However, after 40 days these had increased to 0.0239 mm yr−1 and 0.0017 mm yr−1 respectively. This increase in corrosion rate with time is explained by pitting behaviour. The initial stages of an experiment are dominated by pit initiation and the latter stages by pit growth. In the first instance the surface of the metal is coated with a protective layer of oxide. This is less chemically reactive than unreacted metal, particularly when electrochemical processes are operating since they do not conduct electricity well. Hence, once the oxide layer has broken through and atomic metal is exposed the reaction proceeds more rapidly. As a pit forms, the ability to repassivate spontaneously becomes impossible above a particular size where oxygen cannot diffuse to the new surface exposed in sufficient quantities and only propagation is possible. The pit becomes more anodic compared to surrounding material because of the decreased oxygen concentration within the pit according to the Nernst equation. Hence initiation is relatively slow compared to propagation. There is extensive evidence for pit formation in the analysis by scanning electron microscopy in this paper. Given that experiments in the current work were limited to 270 h, it is unsurprising that our corrosion rates are somewhat slower than those published for longer experiments.

By calculating the absolute rates in units of mol m−2 s−1, it was possible to plot Arrhenius plots for all samples, except mild steel, according to:

\[ \ln(k) = \ln(k_0) - \frac{E_a}{RT} \]

These plots are shown in Fig. 6. Since no mass loss was recordable for mild steel by weighing or ICP, no Arrhenius plot was produced.

Table 3 gives the slope and activation energy derived from Arrhenius plots in Fig. 6 by mass loss and ICP measurements.

There is reasonable correlation between the two techniques used for
Cu and brass, however for Al7075 this is not so since both the mass loss and the ICP measurements contain significant error with only two and three data points available respectively, to calculate the activation energy. This is due to the very low levels of metal loss detected by both techniques. ICP found no Al in solution for Al1050 and only very low amounts of alloying elements for Al7075. The total metal concentration detected by ICP for Al7075 was $< 10\%$ of the mass loss. It is assumed that corrosion products for Al do not enter solution but form solids which do not become distributed in the B100 during normal operation. It is possible that they remain adhered to the metal surface only to be washed away prior to weighing.

3.1. Scanning electron microscopy

SEM studies on both Al1050, Fig. 7, and Al7075, Fig. 8, showed evidence of small, localised and infrequent pits e.g. Fig. 7g shows a pit in Al1050 at 90 °C. The corrosion products on the surface contain C, O and Al and are consistent with salt formation with fatty acids. Fig. 8g shows a similar pit and corrosion products for Al7075 at 110 °C.

With steel coupons, ICP identified no significant amounts of Fe in
solution at any temperature. For the steel coupons, there was no mass loss, rather there was a mass gain, and, in fact, all mild steel samples gained slightly in mass during exposure to B100. Hence the corrosion rate reported was zero by mass method in Fig. 5. SEM studies of mild steel samples, Fig. 9, showed more isolated pits, which also contain C and O, by elemental mapping. An example of steel pit is seen in Fig. 9g at 90 °C. Again, the reaction products are ascribed to insoluble fatty acid formation, hence the slight increase in mass for all steel samples. The mass loss in our experiments was too low to provide realistic corrosion rates for mild steel even though we used higher temperature exposures than those used by Fazal et al [18] which reflects the low corrosion rates of mild steel on exposure to biodiesel.

For Cu and brass samples, Figs. 10 and 11 show significant evidence of metal oxidation in SEM images. For brass, pitting is evident at 100 °C and extensive above this temperature.

In all cases, C and O are present in the reaction products, which fill these pits. The sample at 120 °C showed a more heavily pitted region shown in Fig. 10g which is believed to be due to the flow of B100 across the sample due to stirring. For Cu, pitting occurs at all temperatures and a large pit was observed at 100 °C (Fig. 11g and 11h) filled with reaction products rich in C and O.

In fact, corrosion products rich in C and O were observed for all Cu...
samples across the surface, but in higher amounts in the pits. At 110 °C and 120 °C, pitting no longer dominates for Cu, and a more uniform corrosion reaction occurs across the whole surface. This implies that any copper oxide passivation layers are entirely unstable at these temperatures, with respect to reaction with methyl esters to form the acid and formic acid according to:

\[
\begin{align*}
\text{O} & \quad + \quad 2\text{CuO} \quad \rightarrow \\
\text{O} & \quad + \quad 2\text{Cu} + \text{H}_2\text{O} \\
\text{O} & \quad + \quad \text{H}_2\text{O} \quad \rightarrow \\
\end{align*}
\]

However, the Cu samples showed a much reduced TAN and there is no evidence of free acid or formic acid in the GCMS, so it is reasonable to assume that any acid formed will be in the vicinity of the copper metal, where it reacts readily to form formic acid and fatty acid salts which have been observed in SEM by EDX. The mass loss for Cu matched closely with the ICP results, indicating solubility of Cu salts in B100. Other researchers [37–42] have already shown that Cu is a strong catalyst for double bond oxidation reactions, even at 25 °C, and can form allylic alcohols and epoxy groups, both of which have been detected in GCMS.

The experiments have shown that brass and copper are highly reactive towards B100 and both showed significant corrosion compared to the lower reactivity metals; mild steel Al7075 and Al1050 alloys. For brass, the reaction proceeds via a pitting mechanism at all temperatures and produces a reaction product rich in C and O, which is identified as metal salts of fatty acids. The reaction products vary in size and thickness so the EDX results are qualitative. With Cu, pitting occurs at low temperature, but at higher temperatures a uniform corrosion mechanism dominates and the oxide layer is completely unstable.

For the lower reactivity metals, all showed a tendency to pit and produce fatty acid salts, with a greater tendency to behave like this at higher temperatures.

The corrosion rates calculated are relatively low compared to those from the literature and this is attributable to the short timescale of the study. The initial stages of the corrosion process involve the breakdown of the oxide film on the surface resulting in pit formation. Once a pit has formed, oxidation processes accelerate.

The reaction products from all samples were identified by GC/MS. Without a metal sample present, the B100 underwent auto oxidation and the most reactive species present was shown to be 18.2. With Al1050 and Al7075 present, the reaction products were similar to the blank control experiment, indicating very little interaction of these metals with the oxidative process. However, with mild steel present, it is possible to see evidence of cyclisation of oxidised reaction products and this behaviour is promoted by the presence of Cu and brass metal coupons.

Significant colour changes were observed in biodiesel samples as a result of their contact with brass, copper and steel at temperatures higher than 80 °C. These changes in colour and brightness were related to the presence of metal species in the fuel composition. The colour changes in the fuel resulted from the production of different copper fatty acid salts, or zinc fatty acid salts. There was no evidence for Al, or Fe in B100 from ICP results and it was concluded that, if formed, as indicated by abundance for C and O at pit sites, then these salts are insoluble.

4. Conclusions

Immersion tests for Al7075, Al1050, brass, copper and mild steel at temperatures ranging from 25 to 120 °C in a used cooking oil derived B100 biodiesel showed that:

- Brass (\(< 0.0075 \text{ mm y}^{-1}\)) and copper (\(< 0.08 \text{ mm y}^{-1}\)) corroded at a faster rate than either of the aluminum alloys (\(< 0.0012 \text{ mm y}^{-1}\)) or mild steel (\(< 0.00004 \text{ mm y}^{-1}\)).
- Brass and copper caused chain scission of the biodiesel identified by GCMS analysis to cause changes to the fatty acid methyl ester.
composition as a function of time. Greater changes were found with higher temperature exposure.

- Pitting corrosion of Al1050 and Al7075 were detected by mass loss but ICP was only capable of detecting alloying elements from Al7075.
- No appreciable corrosion was found on the steel alloys by ICP or mass loss.
- SEM analysis showed that corrosion was initiated by a pitting mechanism except for Cu at high temperature which displayed uniform corrosion.
- By mass loss, the activation energies for Cu, Brass, Al7075 and Al1050 were calculated to be $-47.9 \text{ kJ mol}^{-1}$, $-85.4 \text{ kJ mol}^{-1}$, $-90 \text{ kJ mol}^{-1}$ and $-60 \text{ kJ mol}^{-1}$, respectively.
- The activation energies for Cu, Brass, and Al7075 from ICP analysis were calculated to be $-57.9 \text{ kJ mol}^{-1}$, $-87.2 \text{ kJ mol}^{-1}$ and $-140 \text{ kJ mol}^{-1}$, respectively.

Fig. 10. SEM images in SE mode for Brass after 270 h at temperatures of: a) 25 °C, b) 80 °C, c) 90 °C, d) 100 °C, e) 110 °C, f) 120 °C.

Fig. 10g. SEM images in SE mode for Brass after 270 h at 120 °C. More heavily corroded region.
CRediT authorship contribution statement

M. Matbouei: Investigation, Data curation, Writing - original draft.
D.P. Weston: Conceptualization, Methodology, Investigation, Visualization, Writing - review & editing. Xingzhong Liang: Investigation, Data curation. S.V. Hainsworth: Conceptualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Fig. 11. SEM images in SE mode for Copper after 270 h at temperatures of: a) 25 °C, b) 80 °C, c) 90 °C, d) 100 °C, e) 110 °C, f) 120 °C.

Fig. 11g. SEM image in SE mode for Copper after 270 h at 110 °C. More pitted region.
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