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Dearn, Karl; Moorcroft, H; Sukjit, Ekarong; Poapongsakorn, P.; Hu, Enzhu; Xu, Yufu; Hu, Xianguo

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The tribology of fructose derived biofuels for DISI gasoline engines

K D Dearn*[a], H Moorcroft[a], E Sukjit[b], P Poapongsakorn[b], E Z Hu[c], Y F Xu[d] and X G Hu*[d]

[a]Mason Institute of Tribology, Department of Mechanical Engineering, School of Engineering, University of Birmingham, Edgbaston,

Birmingham, B15 2TT, UK

[b]Institute of Engineering, Suranaree University of Technology, 111 University Avenue, Nakhon Ratchasima 30000 THAILAND

[c]Department of Chemical and Materials Engineering, Hefei University, 99 Jinxiu Road, Hefei 230601, PR. China;

[d]Institute of Tribology, Hefei University of Technology, Hefei 230009, P. R. China

Abstract

2-Methylfuran (MF) and 2,5-dimethylfuran's (DMF) combustion characteristics have confirmed their validity as appropriate gasoline replacement and enhancement fuels. However, the performance of fuel injection equipment is dependant on the tribological performance of these fuels Lubricity testing of MF, DMF and their blends with gasoline was undertaken using the high frequency reciprocating rig method, based on ASTM D6079. Results showed that both MF and DMF possessed greater lubricity and wear resistance characteristics than those of gasoline when tested as pure substances. Their blends with gasoline at 2, 4, 6, 8, 10, 20 and 50 percent volume (%vol) showed improved tribological performance also. DMF was found to possess greater lubricating properties than that of MF. As little as 2%vol reduced the wear scar diameter by 46% and 47% for MF and DMF respectively showing even a small addition of these biofuels could greatly improve the tribological performance of the fuel within the engine. This was mainly due to the polar functional groups of MF and DMF bonding to the bearing surfaces during testing, creating a tribo-film that protected the surface, reducing both wear and friction. These effects were greatest for the DMF blends, with two methyl groups leading to stronger polarity and a resulting higher bonding strength to the metal surfaces. The reduction in friction coefficients with the addition of the biofuels showed that utilisation of these blends would reduce frictional losses along the fuel line, improving the overall engine efficiency.

Keywords: 2-Methylfuran, 2,5-dimethylfuran, gasoline, lubricity, HFRR

Highlights

1. Fructose derived MF and DMF biofuels improve the lubricity of commercial gasoline

2. A physicochemical mechanism for the lubricity is proposed

3. The mechanism is reliant on the number of functional methyl groups and the blend ratio

4. **INTRODUCTION**

The tribology of fructose derived biofuels for DISI gasoline engines
* Corresponding authors: (X G Hu) Tel: +86 551 62901359; e-mail: xghu@hfut.edu.cn
             (K D Dearn) Tel +44 121 414 4190; email: k.d.dearn@bham.ac.uk

1

1   As the demand for greater efficiency grows, all areas of energy loss within an engine must be considered. One

2   major factor contributing to engine losses is friction and wear [1]. Regular legislation changes and engine

3   technology developments, such as direct-injection (DI) in spark ignition (SI) engines, push the limits of the

4   physical and chemical properties of the fuels. This is important in the fuel injector equipment as the fuel itself

5   the working lubricant. This is problematic due to the poor lubricating properties of gasoline fuels as a result of

6   their low viscosity and non-polar hydrocarbon compositions. These properties prevent gasoline from developing

7   hydrodynamic and elastohydrodynamic films and leads to poor boundary lubricating properties [2]. These

8   limitations can be improved with the addition of lubricating additives, which are well-developed for diesel fuels,

9   but the technology is much less developed in DI engines. There is some potential for cross cutting between

10   diesel and gasoline additive chemistry. Wei et al. for example, found that a commercially used diesel fuel

11   lubricity additive was also effective at reducing the wear in gasoline fuel [2].

12

13   A number of failures of fuel carrying components in both the automotive and aviation fields led to the

14   requirement to investigate fuel lubricity more deeply. The first large collection of failures occurred during the

15   1960s when both military and civilian aircraft experienced problems with component wear. This was due to

16   more severe refining and increased fuel aftertreatment processes producing aviation fuels with poor lubricity

17   [3,4]. The problems in the automotive industry occurred in the late 1980s and early 1990s where a number of

18   diesel-powered vehicles experienced fuel pump and injector failures. These failures occurred after changes in

19   legislation required large reductions in the sulphur content of fuels. The severe refining process removed

20   aromatic and oxygen-containing compounds within the fuel responsible for its lubricity. This led to increased

21   wear in engine components and ultimately was a significant cause of fuel pump failures [5].

22

23   Research, undertaken by Wei et al. [6,7], into diesel fuel lubricity has shown that polar compounds containing

24   oxygen and/or nitrogen are key to enhancing the lubricating performance of the fuel. However large amounts of

25   these compounds are removed during fuel refining processes required under emissions legislation for

26   automotive fuels. As the legislation for gasoline emissions has changed to become more stringent, a greater

understanding of the fuels lubricating properties is required. In addition to these legislative requirements, more severe techniques used to refine the fuel, as well as new engine designs that require higher pressures within the fuel injection systems [8], place further importance on understanding and improving the fuel's tribological characteristics. As engine technologies have been developed, one in particular, DI, is now a standard configuration for gasoline engines. This requires higher pressures in the fuel pump and injection systems, both of which are lubricated by the fuel itself. Similar to diesel fuels, the sulphur, nitrogen and oxygen content along with the fuel viscosity have all been found to influence the lubricity of gasoline [7,9].

Developing commercial interest in biofuels is part of the drive to reduce global dependence on hydrocarbon fossil fuels. Ethanol is a popular biofuel used as a pure fuel or a fuel enhancement for both gasoline and diesel. It is widely agreed that as a pure substance ethanol has poor lubricating properties and there has been a concern about how it affects the lubricity of fuels when used as a blend. Lapuerta et al. found that the addition of ethanol to biodiesel-diesel blends did not result in significant losses of lubricity until the ethanol concentration neared 100% [10]. Their research also showed that the effects of lubricity reduction by ethanol addition were reduced at higher temperatures due to ethanol evaporation. Agudelo et al. found that the ethanol/gasoline blend E10 had better lubricating properties than pure gasoline and was the optimum blend concentration when considering the fuel's lubricity [8].

2-Methylfuran (MF) and 2,5-Dimethylfuran (DMF) are attractive biofuels according to recent research findings in relation to their methods of production [11,12]. The dehydration and hydrogenolysis of fructose provide a clean process for fuel production, along with other methods including vapour phase hydrogenation [13-16]. The validity of MF as a fuel for SI engines was demonstrated by Wang et al. [17] when they compared the combustion properties of the fuel against gasoline, ethanol, and DMF. MF has a higher indicated thermal efficiency than both DMF and gasoline by some 3% due to its high burn rate. It also has a volumetric indicated specific fuel consumption some 30% lower than ethanol. When burned, MF produces lower levels of particulate matter (PM) [17,18] which is environmentally beneficial and also reduces soot loading in the lubricating oil

within the engine, which if left unchecked can increase the wear on critical components such as bearings, piston rings, etc. [19,20]. Blending MF with gasoline can also improve engine torque and increase the maximum in-cylinder pressure due to a greater burning rate [21].

Hu et al. produced the only study on the lubricity of DMF using a four-ball tribometer [22]. They found that the fuel showed greater wear resistance and lower friction than gasoline and was capable of enhancing gasoline when used as an additive. They suggested oxygen within the molecule contributes significantly to friction induced chemical reactions, leading to greater lubricating properties. An optimal blend ratio of 4% was suggested, although pure DMF had greater lubricity than all blends: However, this test is not representative of the mechanics of the fuel injector pump – similar to that defined in ASTM D6079 [23.24]. MF and DMF both show greater knock suppression than gasoline [17,25] suggesting that they would be appropriate for use in higher compression ratio SI engines. Daniel et al. showed that DMF has higher combustion efficiency than that of gasoline but a lower thermal efficiency due to the higher combustion temperatures [25]. They showed that the engine out emissions produced, with the exception of NOx, are similar to those of gasoline. DMF is most commonly used and tested using DI techniques and has been found to improve the thermal efficiency of a SI engine when used in dual injection testing [26,27].

Although the validity of MF and DMF as suitable fuel replacements in terms of their combustion has been confirmed, the lubricating performance has received little attention. This paper assesses MF and DMF and their blends with gasoline in terms of their lubricity. ASTM D6079, defining a Standard Test Method for Evaluating Lubricity of Diesel Fuels by the High-Frequency Reciprocating Rig (HFRR) has been adapted and used to assess the lubricity of pure MF and DMF, and as a lubricity enhancement blended with gasoline. All have been benched marked against commercial gasoline. This paper provides tribological data confirming the validity of MF, DMF and their blends with gasoline as appropriate automotive fuels.

5.   **METHODOLOGY AND MATERIALS**

1   2.1. Experimental apparatus and conditions

2   Lubricity testing was undertaken using a high-frequency reciprocating rig (HFRR) (PCS Instruments, London, UK).

3   The test conditions are shown in Table 1. This testing method is used to determine the lubricating properties of

4   fuels by means of reciprocating motion of a ball and plate submerged in the test fuel. Information on the

5   operation of this equipment has been extensively covered in literature and can be found elsewhere [for example

6   in 2,6,7,23,24,28,29].

7

8   To allow for gasoline testing the HFRR was adapted by Wei et al. [2] to compensate for the high evaporation

9   rates of the fuel. The adaptations include an increased volume bath to allow for a larger volume of fuel, as well

10 as a PTFE cover to enclose the sample preventing excessive evaporation and contamination. This is important

11 due to the extreme sensitivity of the lubricating properties of gasoline to any contamination in the fuel [2]. The

12 HFRR gasoline conversion kit was supplied by PCS Instruments. A schematic diagram of the HFRR in the gasoline

13 adapted form can be seen in Figure 1. In order to keep the results as relevant as possible, the conditions are

14 taken from the American standard for diesel lubricity testing, ASTM D6079 [24]. This standard is close to the

15 British and European standard, EN ISO 12156-1,2 [29], differing in its allowance of a lower fluid temperature for

16 higher volatility and lower boiling point fuels. Lubricity testing was undertaken at 25 °C as opposed to the 60 °C

17 value used for diesel testing, all else was the same with the exception of the lower specimen conversion bath to

18 compensate for the high volatility fuels. All samples were washed in an acetone solution for fifteen minutes

19 prior to testing and handled only with forceps. This was also the case for any parts of the equipment that came

20 into contact with the fuels tested, after each test. The three fuels initially were all tested in their pure form,

21 followed by a series of blend tests where MF and DMF were blended with gasoline at percentage volumes (%vol)

22 2, 4, 6, 8, 10, 20 and 50. Both MF and DMF readily blend with gasoline negating the need for any complex mixing

23 procedures during preparation. A 15 ml sample size of fluid was used throughout testing to minimise the effect

24 of high evaporation rates of the fuels tested.

25

26 2.2. Fuel physiochemical properties

Reagent grade MF and DMF were purchased from Sigma Aldrich UK. The commercial gasoline was provided by Shell Global Solutions UK. The physical and chemical properties of gasoline, MF and DMF are shown in Table 2. Gasoline is known to contain very small amounts of polar impurities (typically oxygen, nitrogen, and sulphur containing molecules) when compared to diesel fuels [2]. These impurities improve the lubricating properties of diesel fuels suggesting that the lack of these molecules is a large contributing factor to the gasoline's fundamentally poor lubricity. Other important components of a fuel, known to affect the fuels lubricating performance, are aromatics and polar compounds. MF and DMF are partially polar molecules due to the oxygen atoms located within their aromatic ring. The combustion chemistry and confirmation of the validity of the biofuels, MF and DMF, is covered extensively in literature [11,17,18,21,24,25,30-33].

2.3. Analysis of lubrication mechanisms

The lubricity of the fuels was determined by the wear scars generated during testing. For consistency, the methods of measuring the wear scar were carried out in accordance with ASTM D6079. This differs from EN ISO 12156-1,2 in which a corrected wear scar measurement that considers the vapour pressure of the air is made. The wear scar was measured optically using a microscope (Meiji Techno, Somerset, UK) with a 100x magnification lens. During measurement, the major and minor axes of the scar were recorded to the nearest 0.01 mm. These values were then used in Equation 1 shown below to find a wear scar diameter. The surface of the lower test samples was analysed using a 10x magnification lens on a G5 InfiniteFocus (Alicona UK Ltd., Kent, UK) optical 3D microscope. The surface topography of the lower test samples was analysed using a Taylsurf 120 profilometer (Taylor Hobson Ltd, Leicester, UK). Three measurements were taken along the scar, perpendicular to the direction of motion, and an average value acquired.

$$WSD = \frac{M + N}{2} \times 1000 \qquad \textbf{\textit{Equation 1}}$$

Where WSD is the wear scar diameter, M is the major axis of the scar and N is the minor axis of the scar.

1 The surfaces were also investigated using a Zeiss Auriga field emission scanning electron microscope (FE-SEM -

2 Carl Zeiss Microscopy GmbH, Jena, Germany). On completion of the visible wear analysis, surfaces exposed to all

3 three pure fuels during tests were studied using a LUMOS Fourier transform Infrared (FTIR) microscope (Bruker

4 Ltd., Coventry, UK). To see the variation in surface chemistry, a reflective FTIR measurement was taken at five

5 points across each wear scar as shown in Figure 2. The colours at these points match those displayed in the FTIR

6 transmittance spectra presented later in this work. This allowed a comparison of the composition of compounds

7 found within the wear scar, at the wear scar boundary and in the film region.

8

9 **6.   RESULTS AND DISCUSSION**

10 *3.1 Lubricating properties of DMF/gasoline and MF/gasoline blends*

11 The average values of friction coefficient of the pure substances DMF, MF, and gasoline were 0.275± 0.006,

12 0.432± 0.007 and 0.565± 0.01 respectively, showing that both DMF and MF have better lubricity than gasoline.

13 This confirms the findings of Hu et al. [22] with regards to DMF lubricity. Experimental results are shown in

14 Figure 3 and the work undertaken by Hu et al. showed that as little as 2% DMF within the blend was enough to

15 greatly reduce the friction coefficient, improving the antifriction properties of the fuel. It is clear that increasing

16 the %vol of DMF within the fuel beyond 2% has little effect on the lubricity of the fuel as the reduction is only a

17 further 5% compared to the initial drop of 46.5% from 0-2% vol DMF. Similar to the findings of Hu et al. [22]

18 results showed that the presence of DMF greatly enhanced the frictional properties of gasoline at all

19 concentrations tested. The average friction coefficients can be seen below in Table 3. The data suggest that

20 saturation occurs at 2%, as opposed to the value of 10% suggested by Hu et al. in their research. This could be

21 due to the difference in the experimental methods used, strengthening the case for the development of an SI

22 fuel lubricity-testing standard.

23

24 Figure 3b shows the variation in friction coefficient as the %vol of MF increases in gasoline. Although the

25 frictional coefficient of the pure MF was lower than that of gasoline, it's blends with gasoline did not show the

26 same significant drop as seen when DMF was blended with gasoline. The friction coefficient values at 2,4,8,20 %

vol MF were similar to the values measured for gasoline. The lowest friction coefficient in the MF blends was 0.354 ± 0.04 at 6% vol, a reduction of 37.4% against gasoline in comparison to a reduction of 23.6% for pure MF. The average value for friction coefficient for all blends of MF and DMF were lower than pure gasoline, however even the lowest value observed when MF was blended with gasoline was higher than all DMF blends tested. The decrease for MF is less than that seen with DMF suggesting that the frictional properties of MF, although being better than gasoline, are not as good as DMF. The MF/gasoline blends also produced much less stable frictional properties, compared to the DMF blended fuels. Overall however, the greater lubricity of MF and DMF would lead to a reduction in friction losses within the fuel injection equipment, helping to improve the overall engine efficiency [1]. This reduction in friction suggests that both MF and DMF as well as their blends with gasoline would be more suitable for the higher-pressure applications of DISI engines than pure gasoline [8].

3.2. Wear resistance of DMF/gasoline and MF/gasoline blends

The variation in wear scar diameter (WSD) against the %vol of DMF and MF can be seen in Figures 4 a-b. It can be observed that the addition of as little as 2% of either DMF or MF significantly reduced the WSD. Similar to the frictional coefficient findings in DMF, as little as 2%vol within the blend was enough to significantly improve the tribological performance. Adding 2%vol of DMF to gasoline caused a reduction of 47% from an WSD of 793 µm ±7.4 for gasoline to 419±19.8 µm. Increasing the %vol of DMF beyond 2% caused a gradual decrease in WSD up to 20%vol, beyond which increasing the percentage volume had little effect. This is in contrast to the findings of Hu et.al [22] in which they found that the wear resistance of the blend improved up to 4%vol DMF, after which increasing the %vol decreased the wear resistance significantly. This again could be due to the difference in the testing method as one utilises continual sliding motion as opposed to reciprocating sliding used in the other. The reciprocating motion of the HFRR would lead to the lubricating fluid film being repeatedly broken and reformed with each stroke.

The addition of MF to gasoline had a similar effect on the wear resistance of the fuel to that seen during the addition of DMF. The WSD showed a significant reduction of 46% with only a 2% vol addition of MF. The overall

reduction in WSD caused by the addition of MF was less than that experienced when gasoline was blended with DMF with WSD's of 328.75±1.75 µm and 265.5±4.5 µm for pure MF and DMF respectively. The effect of increasing the %vol of MF within the blend had little impact on the WSD when increasing beyond 10% vol. The wear resistance improvement with the addition of MF to gasoline was more significant than the friction reduction. The trends for friction coefficient and wear reduction show little correlation.

The improvement in the friction and wear resistance properties experienced with the addition of both MF and DMF to gasoline can be explained by the polar nature of these biofuels. These polar molecules are able to bind to the material surface, forming a thin tribo-film that acts to separate the material surfaces more effectively, decreasing the interaction and hence reducing both friction and wear. At the saturation volumes of each individual fuel it can be assumed that there is enough of the polar molecules to create a film across the surface and increasing the volume of either MF or DMF past this point has no effect on the film [23]. Reduction in wear experienced as a result of adding MF or DMF to gasoline would lead to increased longevity and reliability of components within the fuel delivery systems.

3.3. Surface topography

Data collected from analysis of the lower sample wear scars generated during testing can be seen in Figure 5. This shows the average depth of the lower wear scar when three profile measurements were taken, perpendicular to the sliding direction. Measurements were made at DMF %vol. of 0, 2, 6, 10, 20 and 100%. On observation of the DMF/gasoline blend data the largest wear scar was generated when testing pure gasoline, correlating to the largest WSD found on the upper samples seen in Figure 4a. At all blend percentages tested, except for 6%vol. DMF, the wear scar depth decreased as blend percentage increased. At 6%vol. DMF there was an unexpected peak in wear scar depth that does not match the WSD or friction coefficient data. Of interest is the increased width of the wear scar generated when testing pure gasoline in comparison to all tests with DMF content within the blend. The wear scar width for pure DMF was less than a third of that seen for gasoline with

1 the addition of 2%vol. DMF reducing the width by approximately 50%. This reduction was considerably larger

2 than the reduction in depth, likely due to the deformation of the ball during testing as material is removed.

3

4 The profile wear scar depth did not follow the same pattern for MF blends with gasoline. The smallest value for

5 wear scar depth, 1.67 μm, was generated at 20%vol. MF, this being the lowest value for all blends tested of MF

6 and DMF. The largest value of wear scar depth, 6.73 μm, was generated at 2%vol. MF. With regards to the wear

7 scar width, the smallest value was generated at 20%vol. MF and the largest is that of pure gasoline. The pattern

8 seen from DMF testing confirms that the pure substance has the best lubricating properties, and that the

9 optimum blend tested was that with the highest percentage volume of DMF. The MF testing however did not

10 match the earlier values measured for WSD and friction coefficients, suggesting that the optimum fuel for wear

11 resistance is the 20%vol. MF blend.

12

13 *3.4. Surface chemistry*

14 Table 4 lists the FTIR spectrum wavenumbers observed when imaging the material surfaces and their associated

15 chemical groups. Due to the atmosphere within which the samples were tested a peak can be seen in all spectra

16 at 2350 cm^{-1}. This was the flex vibration peak attributed to a carbon triple bond [34]. Other peaks observed

17 included those of the hydroxyl (-OH, 3441cm^{-1}, stretching vibration), methyl (-CH$_3$, 2931cm^{-1}, stretching

18 vibration), methylene (-CH$_2$-, stretching vibration) and furan groups as well as carbonyl (-C=O, 1780 cm^{-1}),

19 aromatic carbon (C-C,1400 cm^{-1}) bonds and furanyl (1220 cm^{-1} and 791 cm^{-1}). FTIR spectra for each sample can

20 be seen in Figure 6a-d; the colours signify the position of measurement as shown in Figure 2.

21

22 The Gasoline spectra show that different reactions took place in the surrounding fluid film area, the wear scar

23 boundary and the wear scar centre. In Figure 6(a), the presence of carbonyl compounds and carbon bonds at

24 high intensity with weak peaks signify that methyl and methylene were present in the film area surrounding the

25 wear scar. Carbonyl compounds and hydroxyl groups were also present on the wear scar boundary after the

26 friction process. The wear scar centre did not show any significant spectral wavenumbers, suggesting the surface

1 was clean. This was expected due to the nature of the reciprocating motion of the test essentially polishing the

2 surface. The presence of aromatics in the spectra suggests that the commercial gasoline contained lubricity

3 additives consisting of aromatic compounds.

4

5 The DMF spectra (Figure 6(b)) showed that fewer chemical compounds were present on the material surface

6 after friction. The presence of the hydroxyl group on the wear scar edge was indicative of a friction-induced

7 chemical reaction, that occurred during testing and where alcohol was produced. This confirms the findings of

8 Hu et al. who discovered the presence of alcohol groups within the fuel after friction testing [22]. Aromatic

9 double carbonyl groups, as well as methyl and methylene groups, were all found at the wear scar boundary. No

10 significant chemical findings were made on the rest of the material surface. The scale of the DMF spectrum

11 showed an abundance of these chemical groups was small when compared to the other spectra. The MF

12 spectrum (Figure 6(c)) showed the presence of hydroxyl groups, on a similar scale to that of DMF. The major

13 chemical group present across the entire material surface after friction testing with MF was the furan group. This

14 suggests that MF creates a film layer, binding to the material surface as a result of the polar nature of the

15 molecule, the effect is lessened in the DMF blends.

16

17 The MF /gasoline blend tested (6%vol. MF) (Figure (6d)) shows a much greater variety of compounds on the

18 material surface as well as a greater intensity. Presence of the furan group was shown at the wear scar centre

19 and boundaries, but not in the surrounding film area. Aromatic carbonyl compounds and carbon bonds were

20 present across the entire material surface. This is similar to that seen for pure gasoline with the exception of the

21 wear scar centre. Methyl, methylene and hydroxyl groups were observed across the material surface. From the

22 spectral data it is clear that a greater variety of chemical compounds are present on the material surface after

23 friction testing including gasoline, which contained a number of performance enhancing additives. The best

24 lubricant determined from the friction testing was DMF and it is clear from the spectral data that DMF has the

25 lowest transmittance intensity showing that the abundance of chemical compounds on the material surface is

considerably lower than the other fuels tested. This shows that the lubricating film created by DMF during testing provides the best protection to the material surface.

3.5 Wear and lubrication mechanisms

The wear scar on the disc specimens were also observed using an FE-SEM and results are shown in Figure 7. The specimen tested in the pure gasoline tests (Figure 7 (a)) had a large wear scar with severe abrasive grooves, synonymous with the poor lubricity of gasoline. Wear scars on the specimens tested in MF and DMF, shown in Figure 7 (b) and (c), were smaller than those tested in pure gasoline. It is known that organic compounds such as furans can adsorb on to metal surfaces and then form tribo-films to lubricate the surfaces. However, during the rubbing process, the film can be destroyed. Previous studies have shown that the aromatic ring of furan is usually adsorbed parallel to metal surfaces [35-37], as is illustrated schematically in Figure 8. With two methyl groups, DMF is likely to have stronger polarity and higher bonding strength to the metal surfaces than MF which has only one methyl group. As a result of this, the DMF tribo-film with stronger polarity, would provide a more robust lubrication regime and protect the surface of specimens from wear. This is why a smaller and smoother wear scar was observed on the specimens tested in DMF (Figure 7 (c)). Figure 7 (d) and (e) show wear scars of specimens tested in the blends of 6%vol. MF and 6%vol. DMF, respectively. It can be seen that blending DMF to gasoline significantly reduced abrasive wear (Figure 7 (e)). However, due to the weak bonding strength between the MF tribo-film and the metal surface, the MF failed to protect the metal surface; and evidence of abrasion was found (Figure 7 (d)).

7.   CONCLUSIONS

Both 2-methylfuran (MF) and 2,5-dimethylfuran (DMF) have better lubricating characteristics than gasoline. DMF was found to be a better lubricant than MF both in terms of its frictional properties and wear resistance. The following conclusions from this study can be drawn:

1)   Both pure MF and DMF showed better frictional properties than gasoline. At all %vol. blends greater than 0, the presence of both MF and DMF improved the lubricity of the fuel. At 10% vol DMF the blend was stable,

following with increasing the percentage volume having a minimal effect on the blends lubricity. From the data collected the MF/gasoline blends cannot be considered as stable with regards to the frictional properties.

2)   Wear resistance of MF and DMF is considerably better than that of gasoline with all blends also proving favourable. The blends stabilised at 10% and 20% for MF and DMF respectively, at which percentage volumes the blends can be considered saturated. From this point, increasing the percentage volume further had minimal effect on the tribological performance.

3)   Pure DMF has optimum lubricating properties, with the lubricating properties of its blends with gasoline improving with the increase in DMF concentration. For both DMF and MF the optimum blend with gasoline is 6%vol., when forming a compromise between frictional properties and wear resistance.

4)   Comparably low transmittance intensity of compounds found on the material surface after friction testing shows that both MF and DMF generates a furan based tribo-film on the surface. It is DMF that forms the most effective lubricating film to protect the surface, as a result of the highly polarised, two methyl groups.

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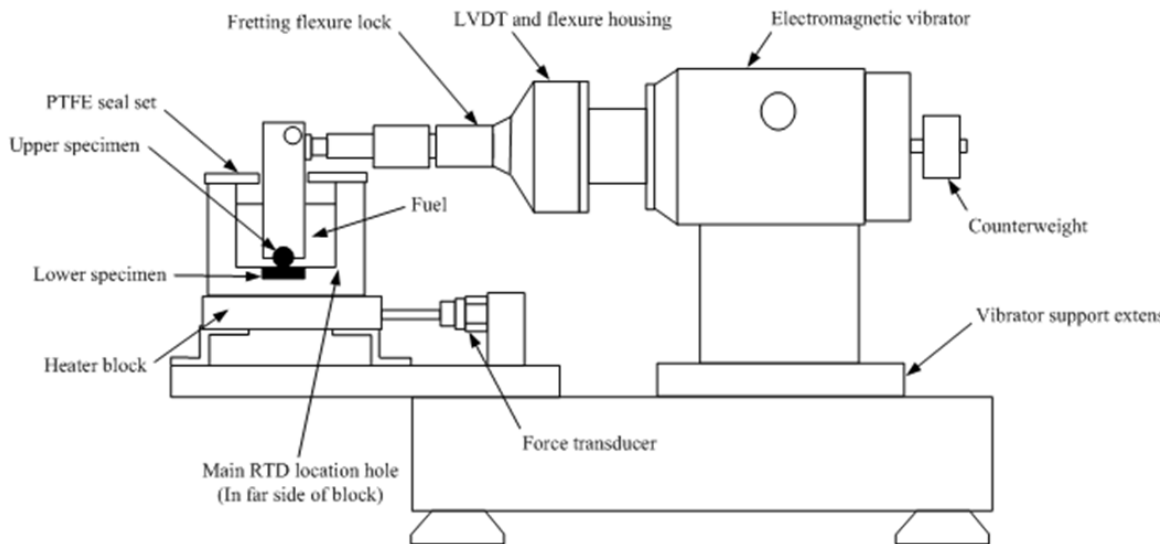
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Figure 1: Schematic diagram of a HFRR modified for gasoline testing.

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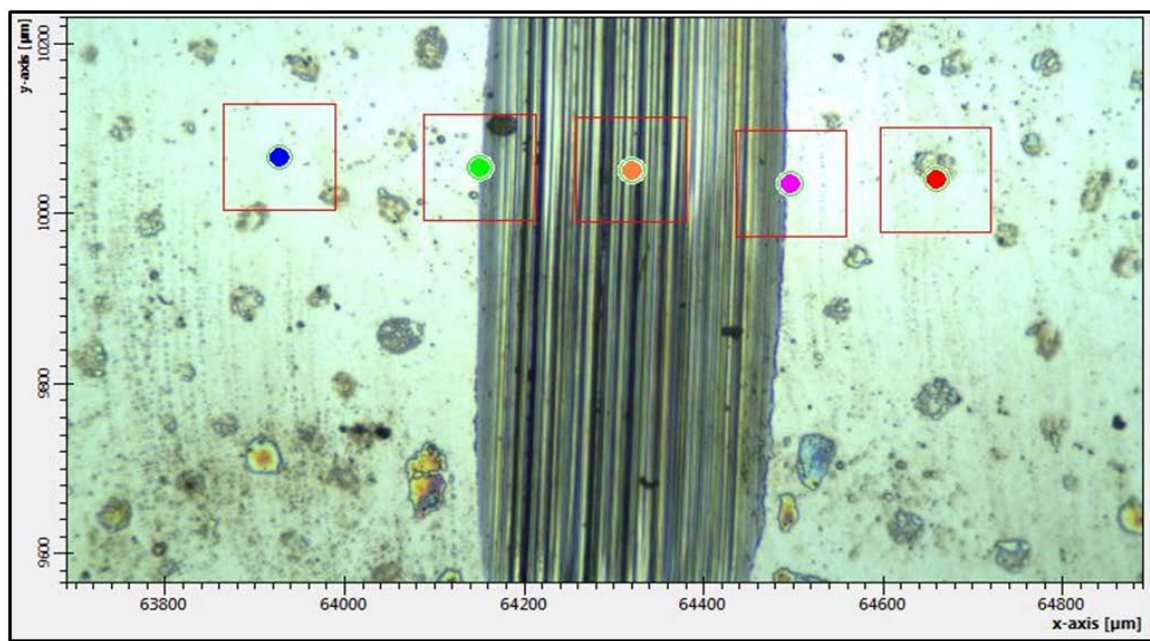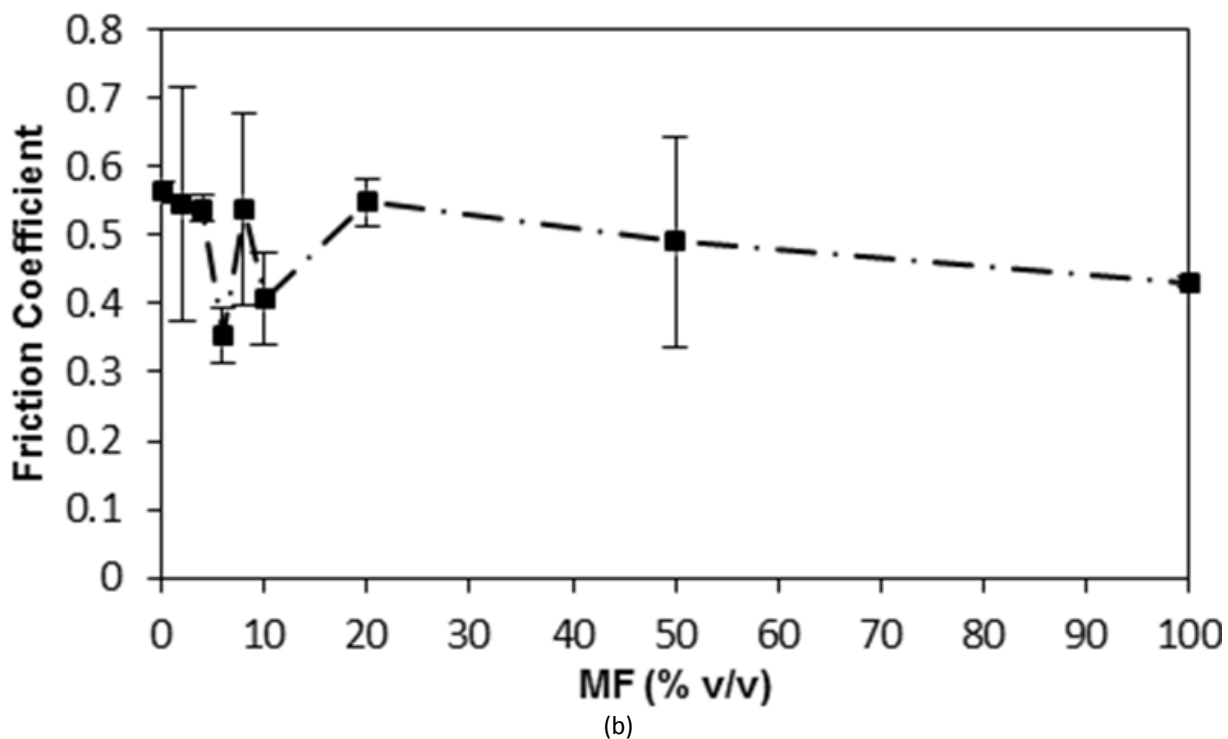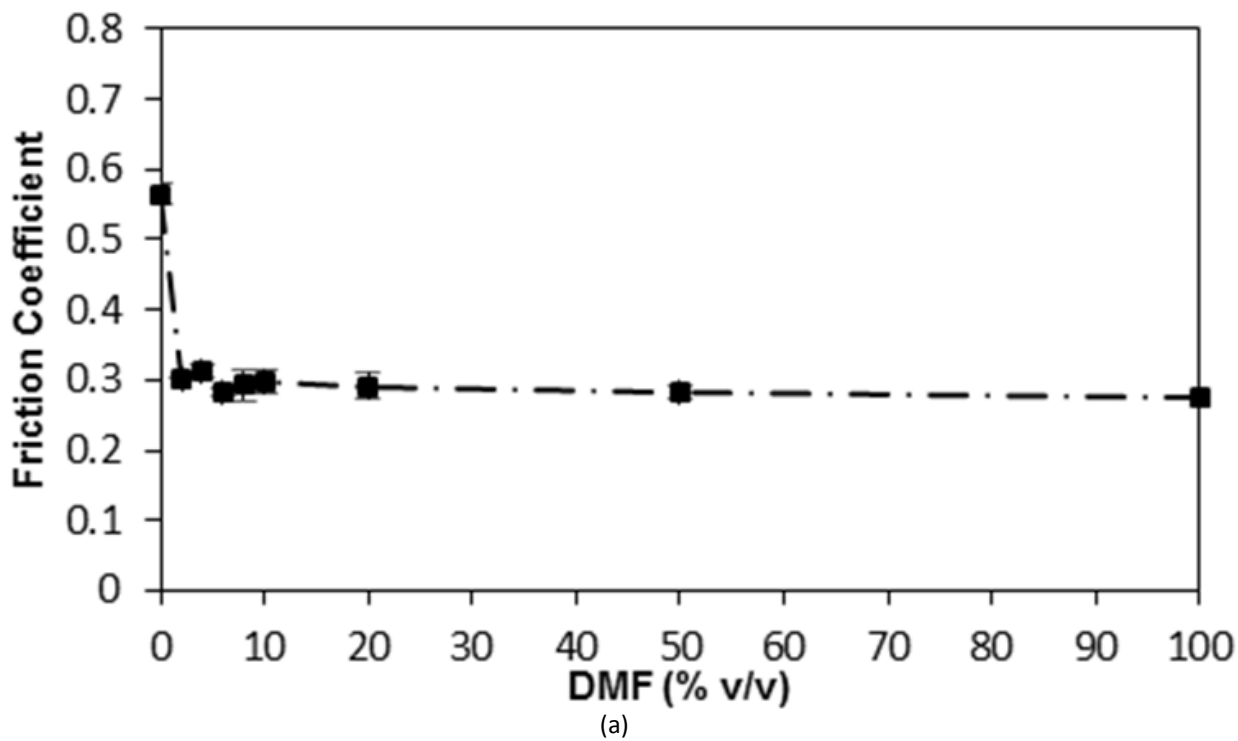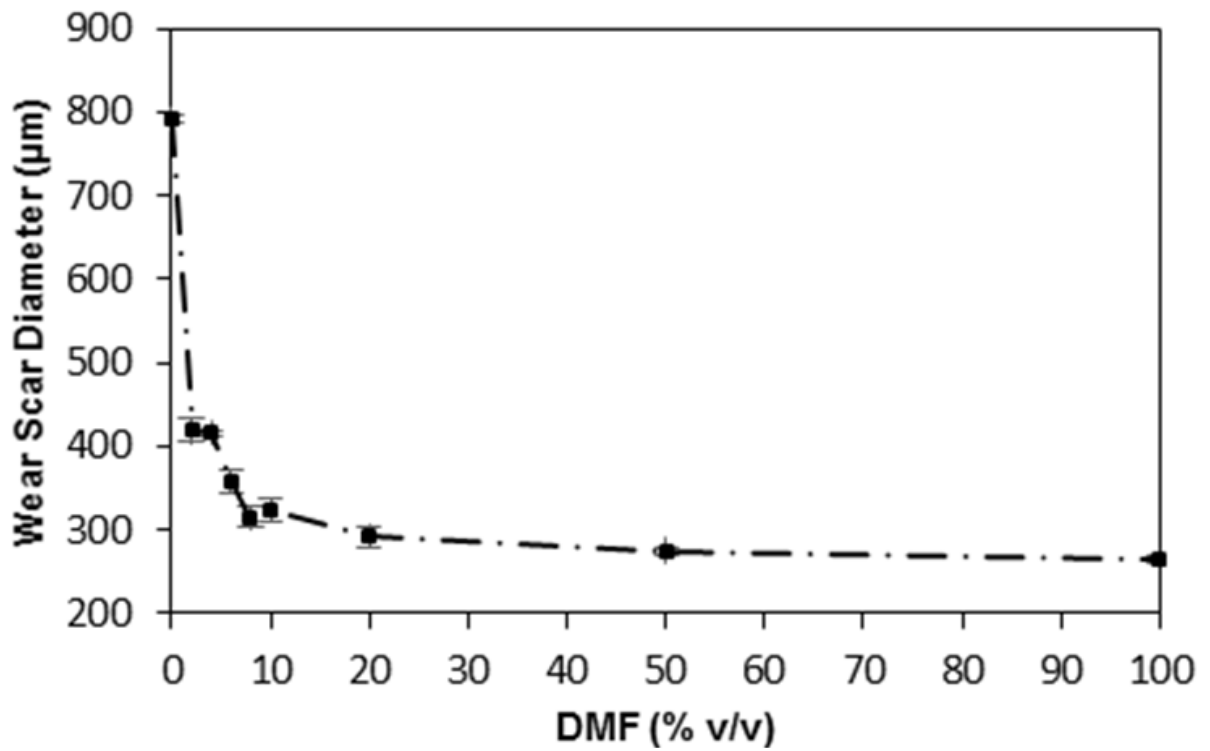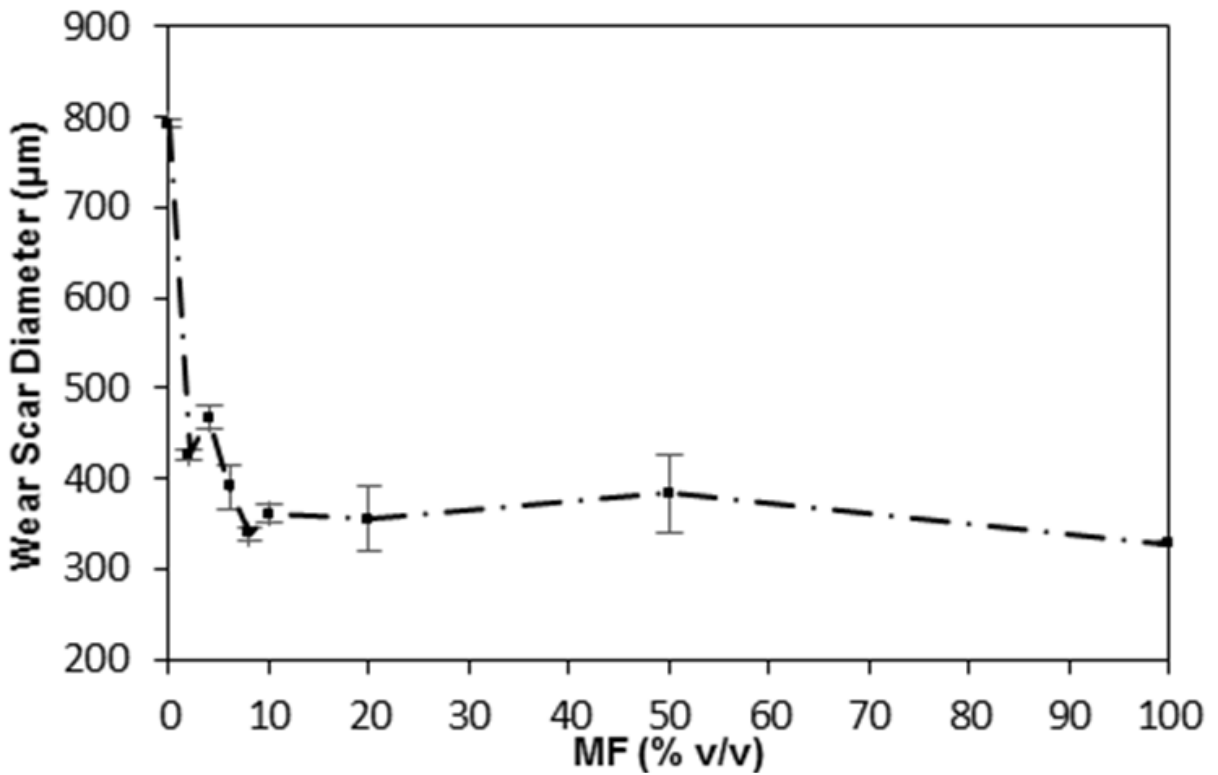**Figure 2:** FTIR microscope measurement locations (DMF100).

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Figure 3: Variation of the friction coefficient as the volume percentage of (a) DMF and (b) MF within the blend increases.

1

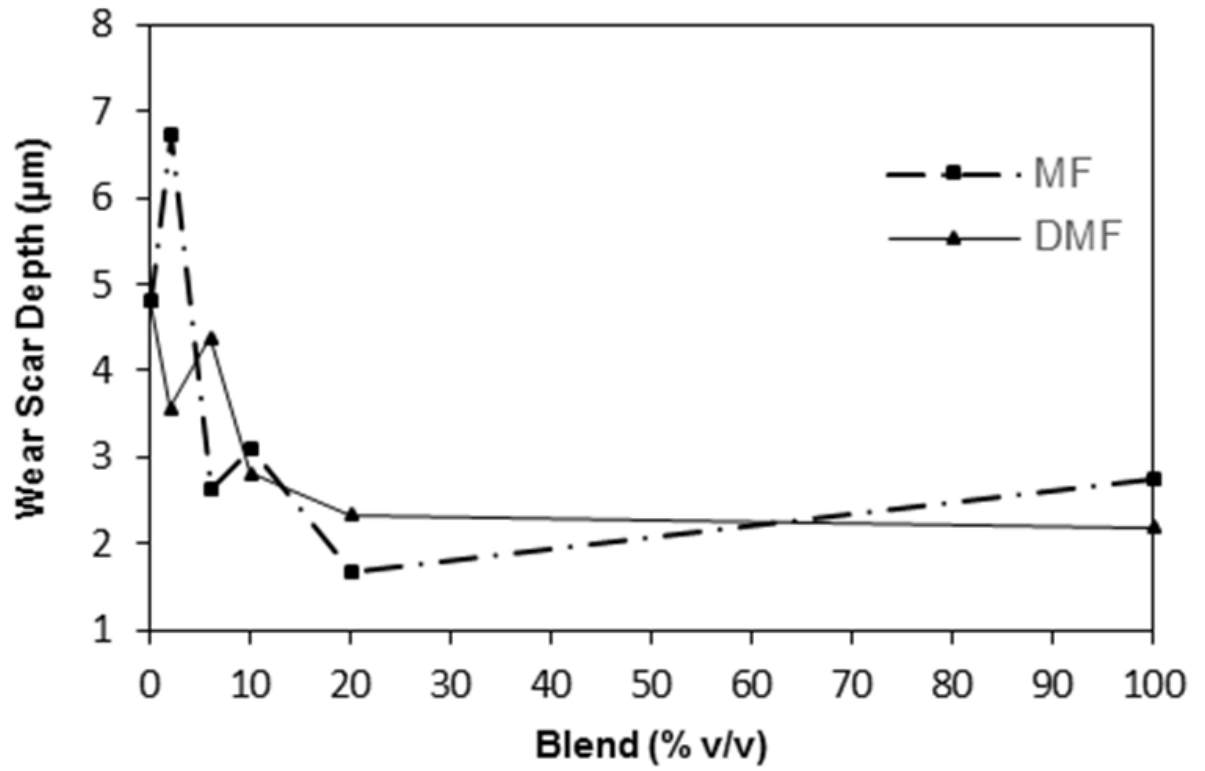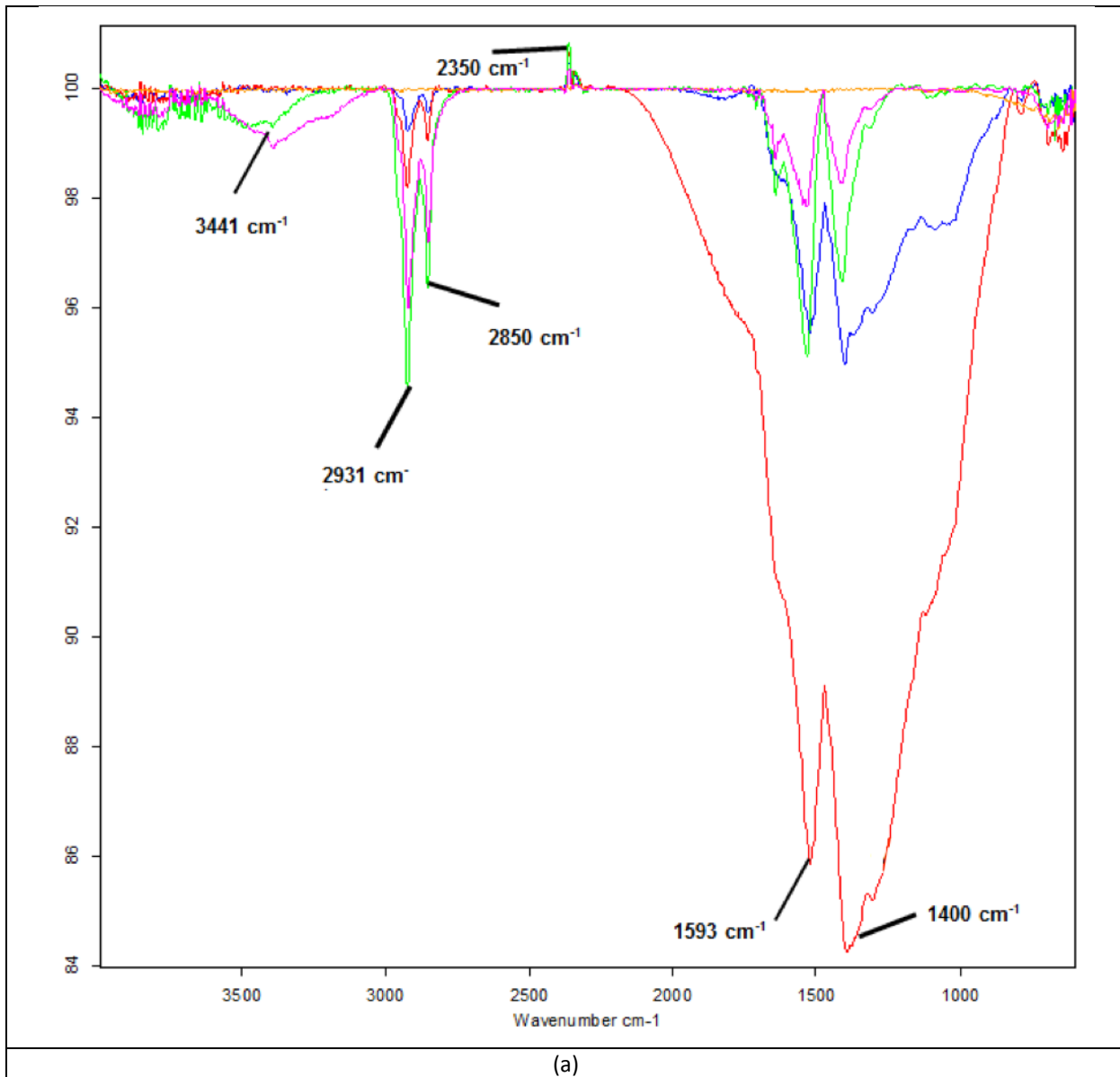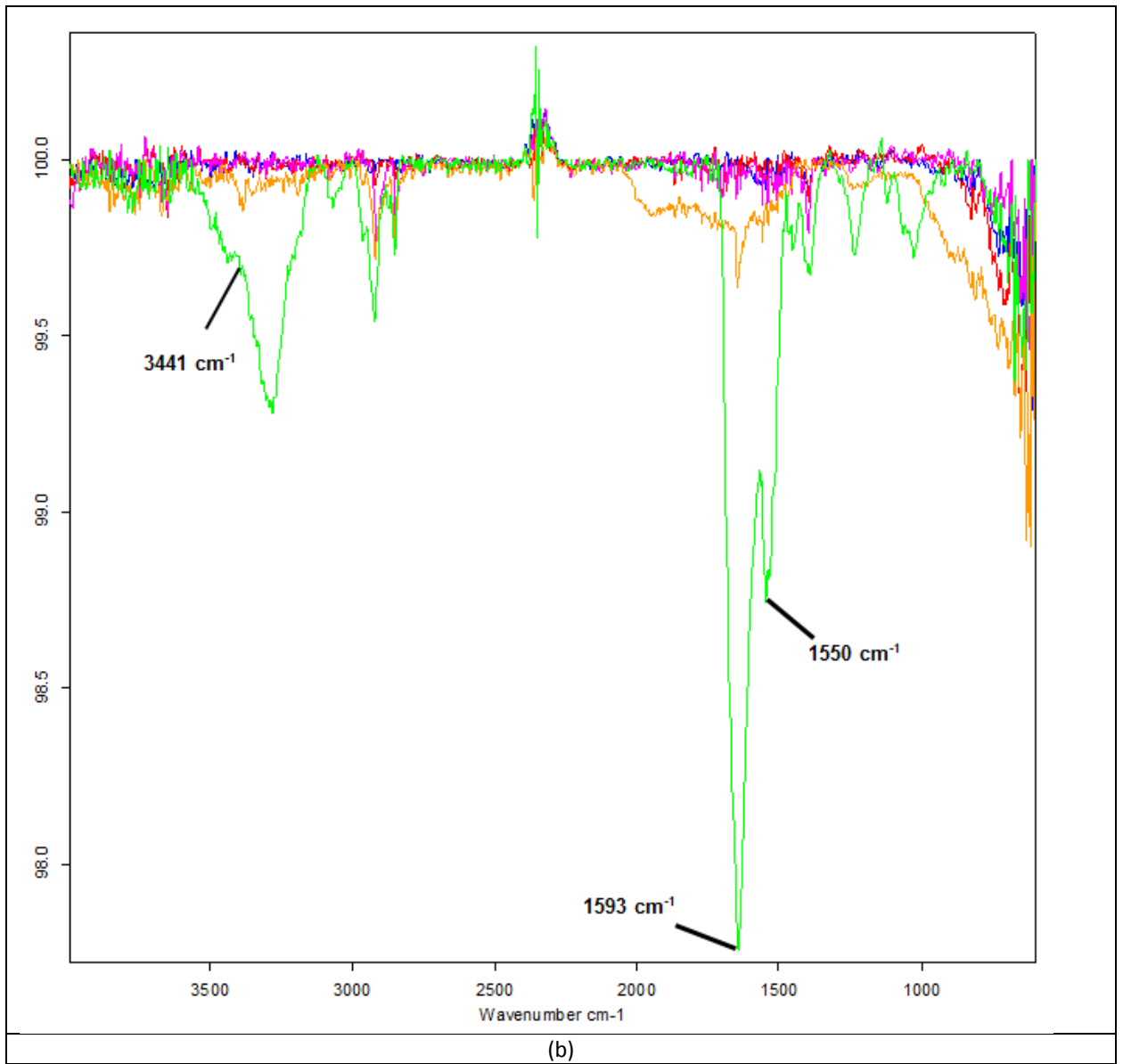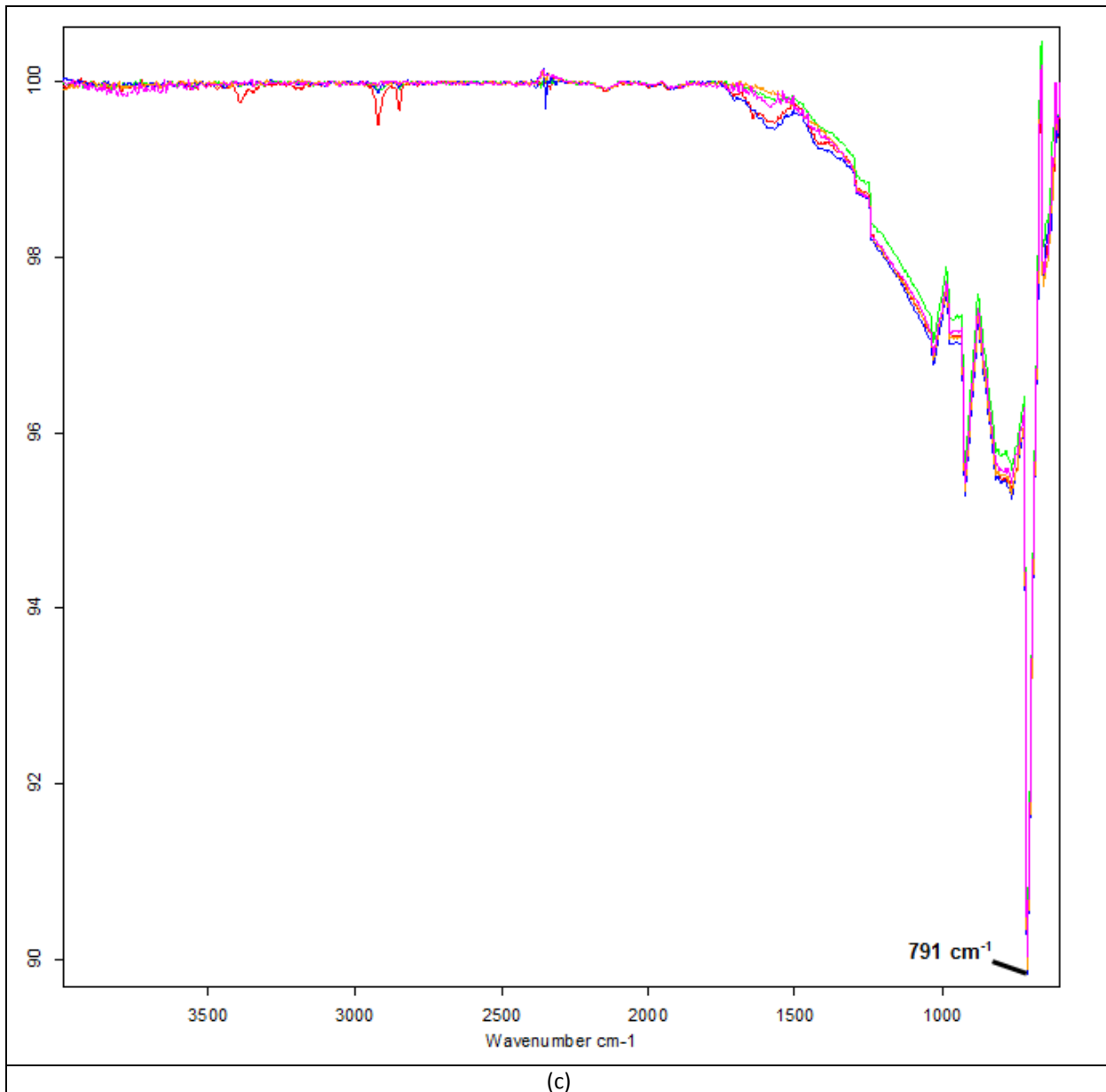**Figures 4**: Variation in WSD with increasing percentage volume of (a) DMF and (b) MF.

1

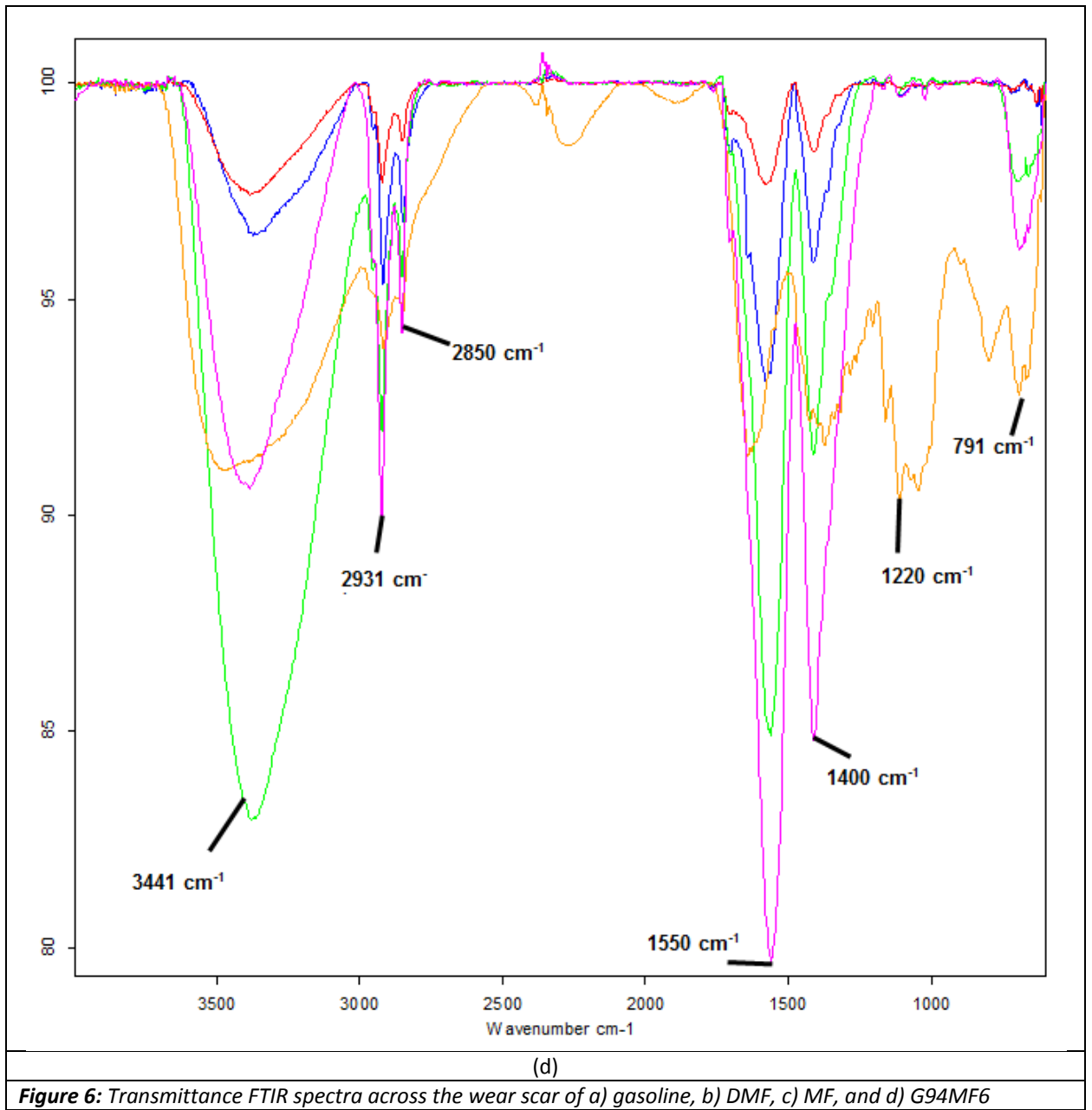**Figure 5:** Effect of increasing blend percentage on wear scar depth.

2

(a)

(b)
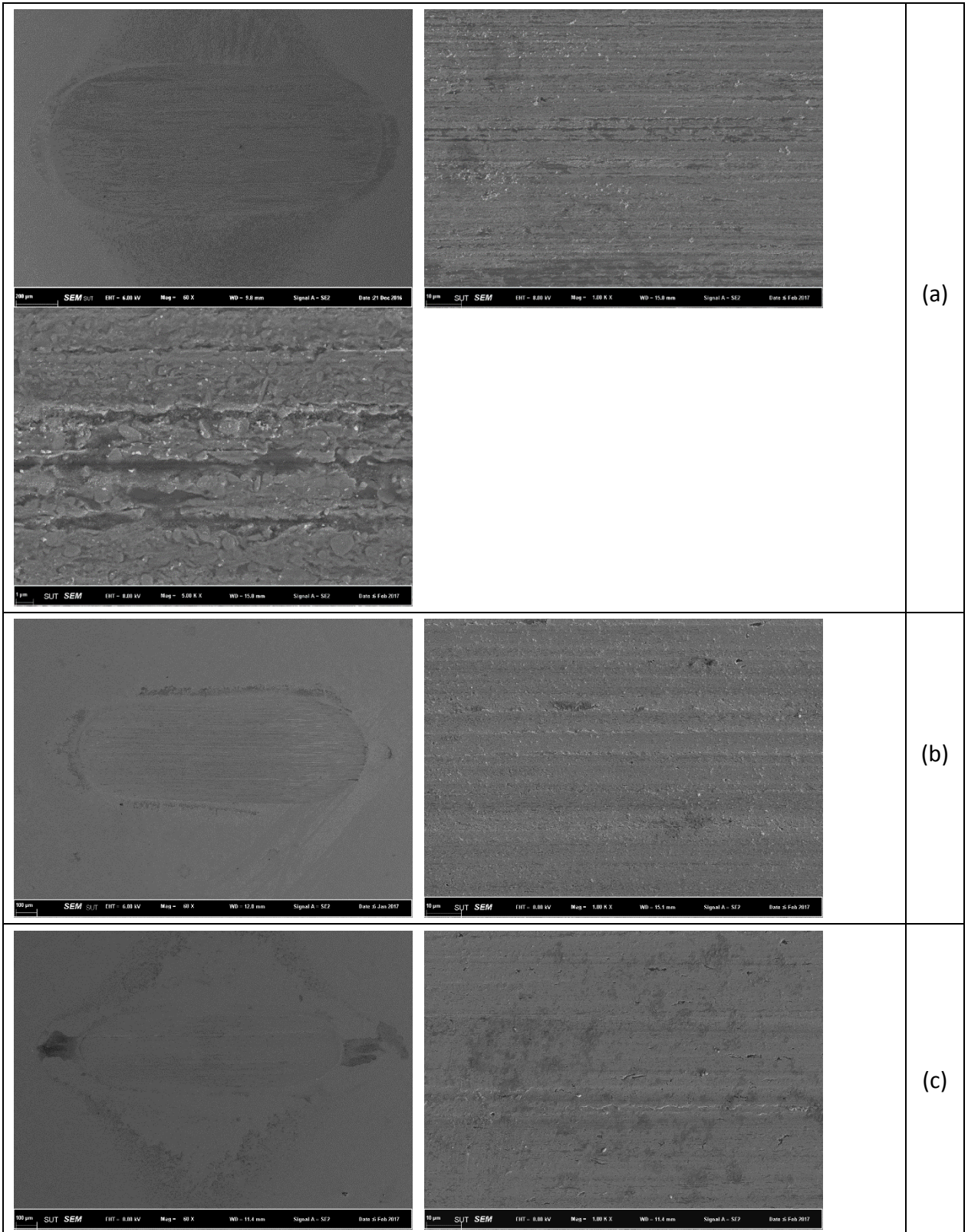
(c)

Figure 6: Transmittance FTIR spectra across the wear scar of a) gasoline, b) DMF, c) MF, and d) G94MF6

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2

1

(a)

(b)

(c)

Figure 7: SEM micrographs of disc specimen tested in (a) Gasoline, (b) MF, (c) DMF, (d) G94MF6, and (e) G94DMF6
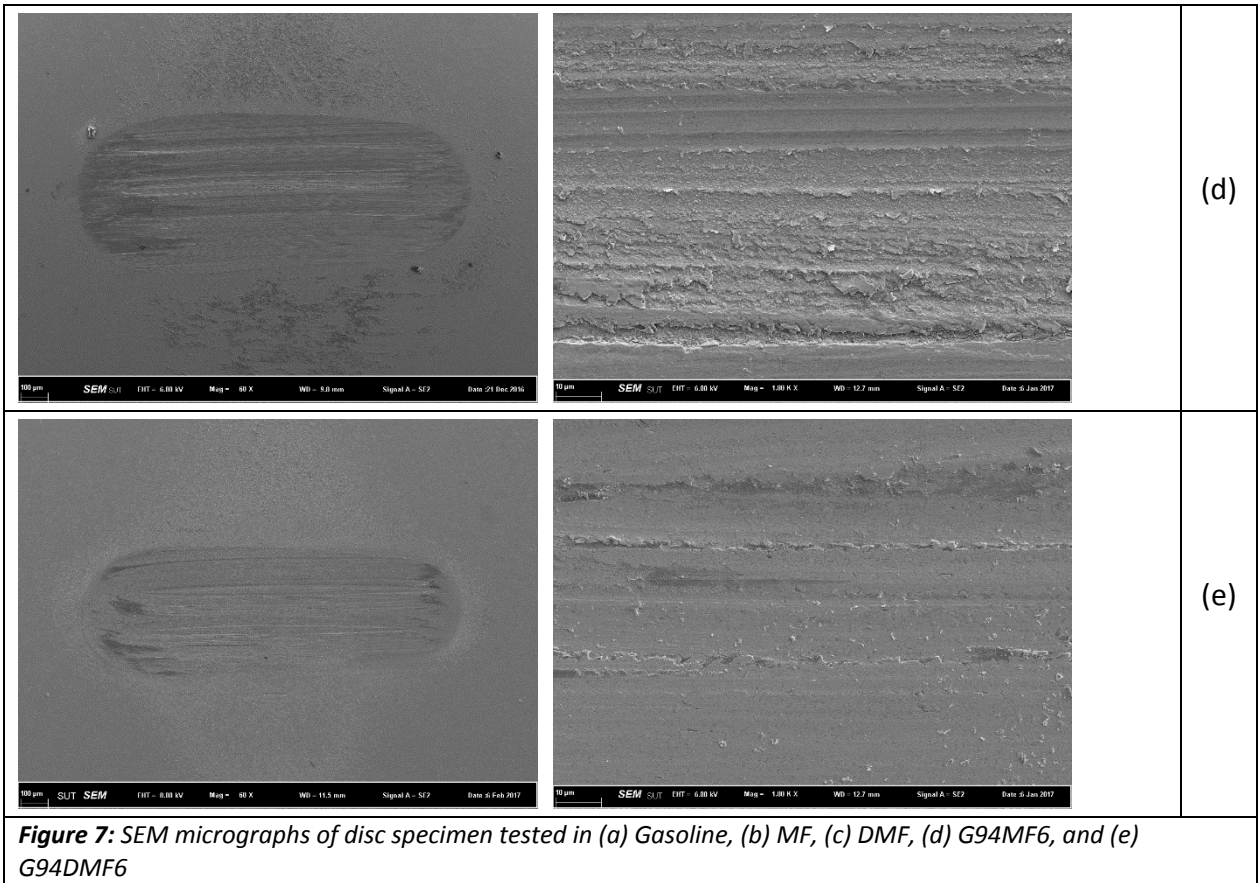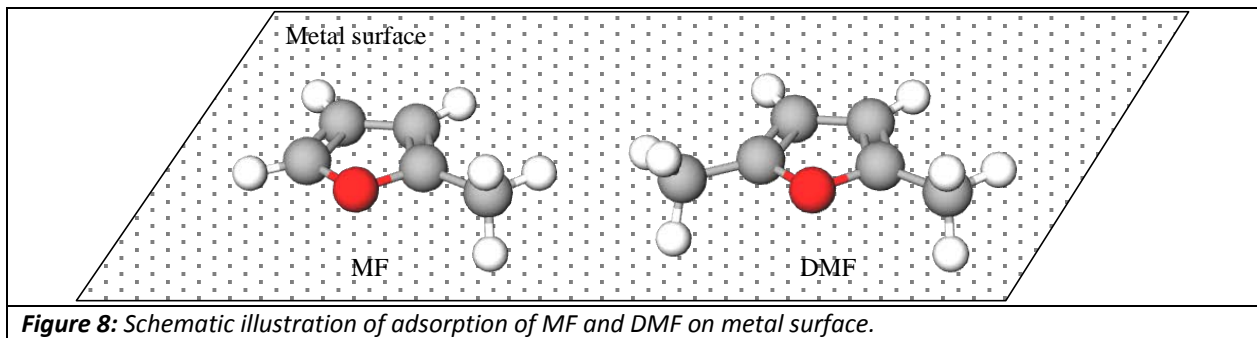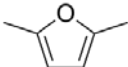
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Figure 8: *Schematic illustration of adsorption of MF and DMF on metal surface.*

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1　　**Table 1:** Main test conditions of HFRR fuel test[a]

Condition	Value
Stroke Length	1 ± 0.02 mm
Stroke Frequency	50 ± 1 Hz
Load	200 ± 1g
Test Duration	75 ± 0.1 min
Fluid Volume	15 ± 0.1 ml
Fluid Temperature	25 ± 2°C
Ball Properties	6 mm diameter. AISI 52100 Steel
Disc Properties	10 mm diameter. AISI 52100 Steel

2　　*[a] – Based on ASTM D6079 [28]*
3
4　　Table 2: Properties of fuels tested[a]

	Gasoline	MF	DMF
Molecular formula	$C_2 - C_{14}$	C_5H_6O	C_6H_8O
Density at 20°C (kg/m^3)	744.6	913.2	889.7
Research octane number (RON)	96.8	103	101.3
Motor octane number (MON)	85.7	86	88.1
H/C ratio	1.795	1.2	1.33
O/C ratio	0	0.2	0.167
LHV (MJ/kg)	42.9	31.2	32.89
LHV (MJ/L)	31.9	28.5	29.3
Gravimetric oxygen content (%)	0	19.51	16.67
Heat of vaporization (kJ/kg)	373	358.4	332
Flash point (°C) [b]	-40	-22	1
Initial boiling point (°C)	32.8	64.7	92.0

5　　*[a] – Information taken from [17]*
6　　*[b] – Information taken from [33]*

7

8　　Table 3: Average friction coefficient data

Blend %vol. with Gasoline	Average Friction Coefficient					
	DMF			MF		
0	0.565	±	0.015	0.565	±	0.015
2	0.302	±	0.000	0.544	±	0.170
4	0.313	±	0.009	0.539	±	0.019
6	0.283	±	0.004	0.354	±	0.040
8	0.293	±	0.023	0.539	±	0.140
10	0.297	±	0.017	0.407	±	0.068
20	0.292	±	0.020	0.548	±	0.034
50	0.284	±	0.010	0.491	±	0.152
100	0.275	±	0.001	0.432	±	0.007

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1   Table 4: The wavenumbers corresponding to the main groups identified on the material surface

Wave number (cm^{-1})	Corresponding to groups
3441	-OH
2931	$-CH_3$ (stretching vibration)
2850	$-CH_2-$ (stretching vibration)
2350	$-CO_2$
1780	C=O (carbonyl)
1593	$-CH_3$ (bending vibration)
1550	$-CH_2-$ (bending vibration)
1400	C-C (aromatic)
1220, 791	