Tribology International 55 (2012) 119–125

Contents lists available at SciVerse ScienceDirect

Tribology International

journal homepage: www.elsevier.com/locate/triboint

On the fundamental lubricity of 2,5-dimethylfuran as a synthetic engine fuel

Enzhu Hu [a], Xianguo Hu [a,*], Xiangyang Wang [a], Yufu Xu [a], Karl D. Dearn [b,**], Hongming Xu [a,b]

[a] Institute of Tribology, Hefei University of Technology, Hefei, Anhui 230009, China
[b] School of Mechanical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

ARTICLE INFO

Article history:
Received 11 August 2011
Received in revised form
24 May 2012
Accepted 6 June 2012
Available online 15 June 2012

Keywords:
2,5-Dimethylfuran
Gasoline
Lubricity

ABSTRACT

2,5-Dimethylfuran (DMF) as a new synthesis alternative engine fuel has received much attention in terms of its production and combustion characteristics. However there is a distinct lack of information available on the tribological properties of DMF, and more specifically, its lubricity. In this paper the lubricity of DMF was studied using a four-ball tribometer. The results show that DMF has better antiwear and antifriction properties than commercial gasoline. The lubrication properties of gasoline/DMF blends of 2–20 vol% have been examined in this paper. It has been found that 4 vol% DMF in gasoline is optimal for reducing friction and improving the wear resistance.

1. Introduction

The increase in research conducted into alternative fuel sources is driven not only by the impact that hydrocarbon fossil fuels (HCFF) have on the environment, but also the depletion of HCFFs and the subsequent rise in the price of petroleum products [1]. There are many alternative fuels to HCFFs under investigation including ethanol, biofuels and dimethyl ether (DME). However, the properties and cost of these alternative fuels can restrict their practical application. Ethanol, when blended with gasoline, has a low energy density, a high volatility and high water absorptivity, leading to high total hydrocarbon (THC) emissions after combustion [2]. Biofuels cover a range of alternative fuels which can be produced from plant seed and vegetable oils as well as animal fats. Biofuels can be limited by poor low-temperature performance and oxidation stability, high NO_x emissions [3,4], high cost and difficulties in supply. DME is a syngas derived alternative fuel which emits zero particulate emissions when burnt in its pure form and decomposes into methane, hydrogen and carbon monoxide. The limitations associated with DME are low viscosity (an order of magnitude lower than petroleum fuels), high volatility, high chemical corrosivity and poor lubricity [5].

2,5-Dimethylfuran (DMF), a new synthetic energy fuel has been developed in light of the limitations associated with the existing alternative fuels [6]. In comparison to ethanol, DMF has a 40% greater energy density, a 20 °C higher boiling point and a higher octane number. DMF is insoluble in water but readily blends with gasoline and can therefore act as an octane promoter in gasoline. Román-Leshkov et al. synthesised DMF from fructose biomass using a two-step catalytic technology [7]. Firstly, an acidic catalyst was used to convert fructose into the intermediate product 5-hydroxymethylfurfural (HMF), following this a copper–ruthenium catalyst was used to convert HMF into DMF. This development allows the production of DMF on a larger scale. Further developments have included Zhao et al. who recently reported a catalytic-synthesis method for producing HMF with a highest yield of about 70% [8].

At present, studies concerning the application of DMF have focused mainly on aspects of pyrolysis and its combustion. Grela et al. studied the low pressure pyrolysis of DMF at low-temperatures (between 777 and 977 °C) [9]. Reactants were heated in a steady flow reactor and the products were analysed using a mass spectrometer. It was concluded that the reaction to produce CO was also the main reaction for the pyrolysis of DMF. Wu et al. used tunable vacuum ultraviolet (VUV) synchrotron radiation photoionization and molecular-beam mass spectrometry to identify the combustion intermediates in a low-pressure premixed laminar 2,5-dimethylfuran/oxygen/argon flame with an equivalence ratio of 2.0 [10]. More than 70 species were detected including furan and its derivatives, aromatics, and free radicals. Zhong et al. studied the performance of DMF in a gasoline direct injection (GDI) engine [11], concluding that the combustion characteristics and emissions were similar to those of gasoline. To date however, there are no reported studies on the lubricity of DMF as an engine fuel. This paper provides fundamental tribological data for the potential application of DMF as engine fuel and other potential applications of DMF in the energy industry.

* Corresponding author. Tel.: +86 551 2902956.
** Corresponding author. Tel.: +44 121 414 4190.
E-mail addresses: xghu@hfut.edu.cn, tribohu@gmail.com (X. Hu), k.d.dearn@bham.ac.uk (K.D. Dearn).

0301-679X/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.triboint.2012.06.005

2. Materials and methods

A summary of the materials and experimental apparatus used in the study is shown in Table 1. Gasoline was purchased from Hefei Petrochemical Co. The pure DMF was purchased from Zaozhuang Chemical Co. Ethanol, acetone, and other chemical reagents were purely analytical. The steel balls with the standard diameter 12.7 mm were purchased from Hefei Bearing Co. The main materials and apparatus used in the study are shown in Table 1. The pure DMF and gasoline were ultra-filtered using a 0.5 μm quartzose-film to remove any other possible impurities. The properties of the DMF and gasoline were evaluated after filtration according to the standards shown in Table 2 along with the physical and chemical properties of DMF and gasoline. It can be seen that DMF has a higher flash point and lower sulphur content than gasoline, and also a higher extreme pressure value.

Table 1
Materials and apparatus.

Materials and apparatus	Specification	Manufacturer
Ball bearing steel AISI 52100	Φ12.7 mm	
		Hefei Bearing Co. China
	HRC 59-61	
Four-ball tribometer	MQ-800	Jinan Shijin Group Co.
Optical microscope	LY-WN-HPCCD	Chengdu Liyang Electronics and Hi-Tech Components Ltd.
DMF	Chemically pure	Zaozhuang Chemical Co., Shandong
Gasoline	93#	Hefei Petrochemical Co. SINOPEC

The significance of # is the different grade of gasoline products which were used in China.

Table 2
Physical and chemical properties of filtered DMF and gasoline.

Item	DMF	Gasoline	Method
Density at 20 °C (kgm^{-3})	906	746	EN ISO 12185
Viscosity at 40 °C (mm^{2}s^{-1})	0.525	0.469	EN ISO 3104
Acid value (mg KOHg^{-1})	0.0531	0.0162	EN 14104
Flash point (°C)	0	−38	EN ISO 3679
Water content (mgkg^{-1})	Trace	Trace	EN ISO 2160
Total contamination (mgkg^{-1})	0	0	EN 12662
Sulphur content (mgkg^{-1})	2	17	EN ISO 20846
Copper strip corrosion at 50 °C for 3 h (grade)	1	1	EN ISO 2160
Extreme pressure (N)	333	274	ASTM D2783

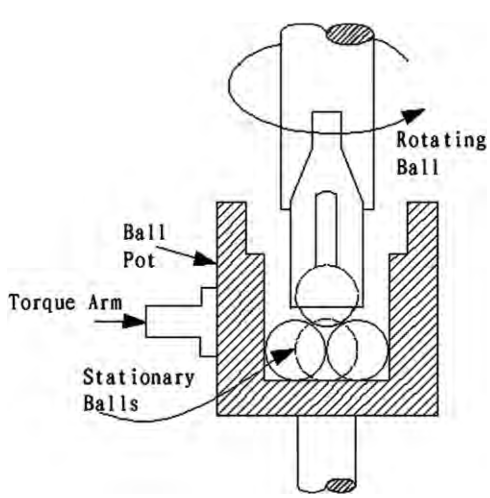


Fig. 1. Schematic diagram of four-ball tester.

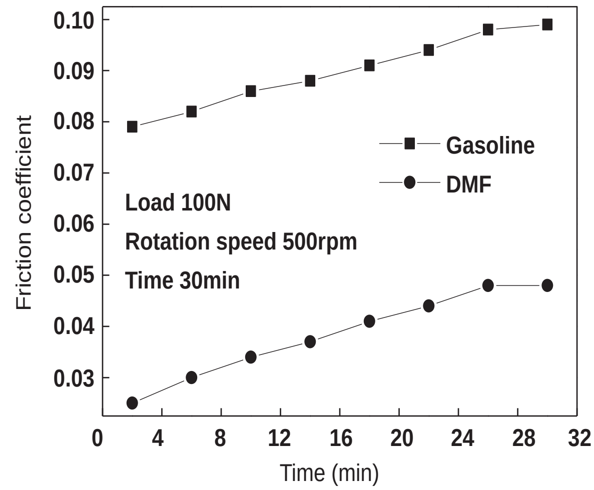


Fig. 2. Relationship between the friction coefficient of gasoline and DMF with contact time.

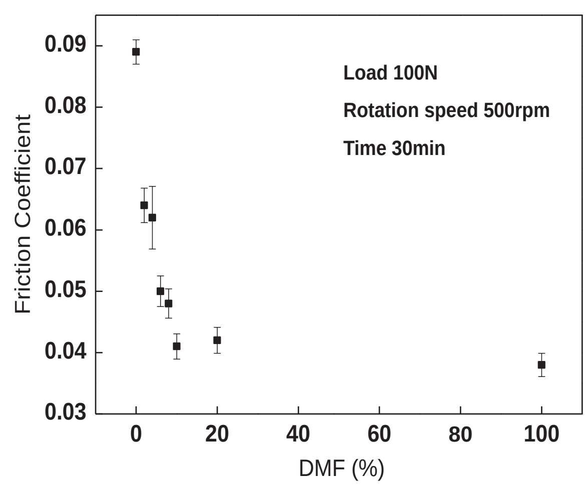


Fig. 3. Variation of average friction coefficient of gasoline blended with DMF in increasing volume.

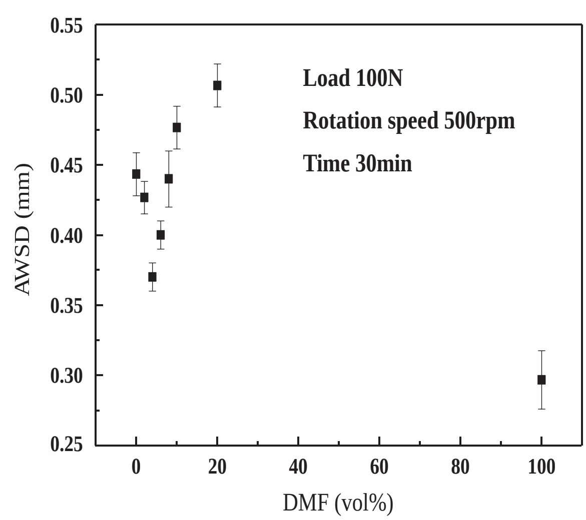


Fig. 4. Effect of DMF on the wear resistance of gasoline.

This implies that DMF has excellent load-carrying capacity and good extreme pressure properties [12,13]. The acid value and viscosity of DMF are also higher than those of gasoline. Other properties in Table 2 between DMF and gasoline are similar.

At present, there are three main methods to evaluate the lubrication properties of fuel, viz. the high frequency reciprocating rig (HFRR) [14–16], scuffing load ball-on-cylinder lubricity evaluator (SLBOCLE) [17] and the four-ball test machine method

Table 3
Average wear scar diameters and images of the steel ball surface after rubbing for 30 min under different DMF concentrations.

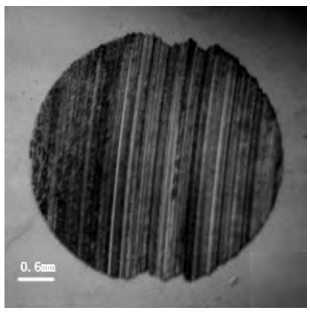
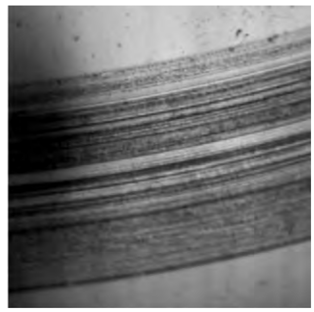
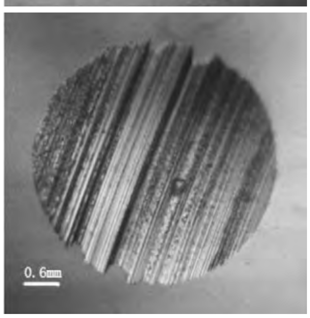
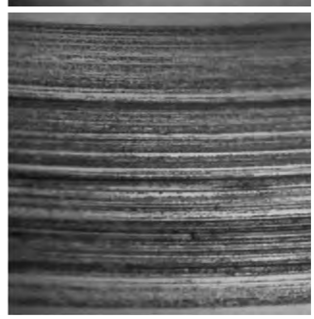
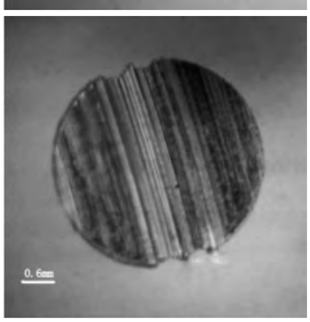
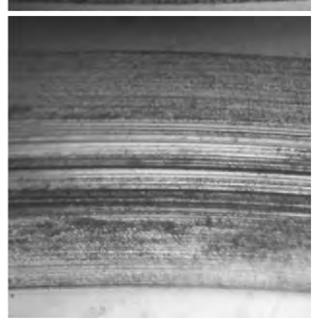
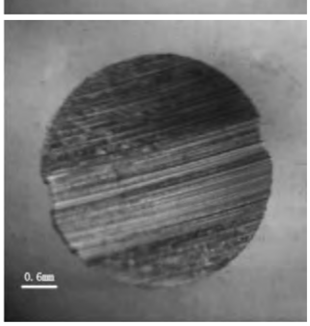
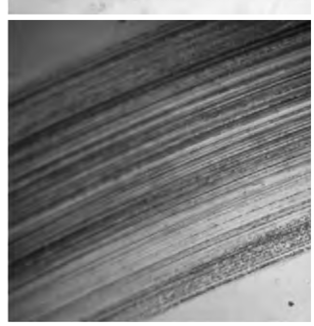
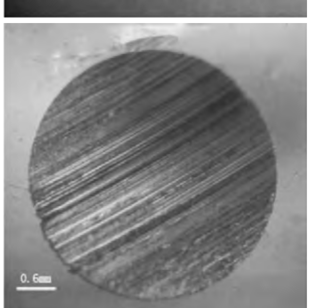
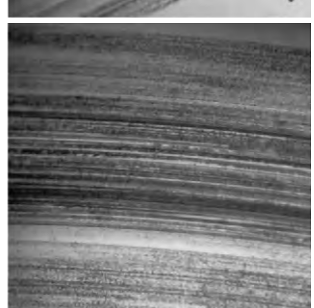
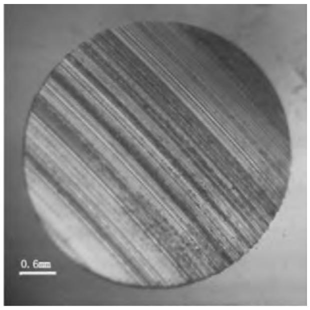
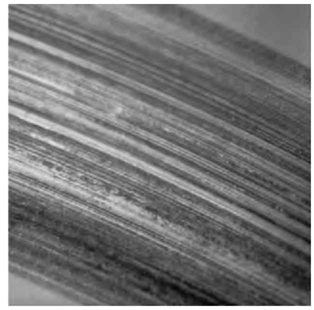
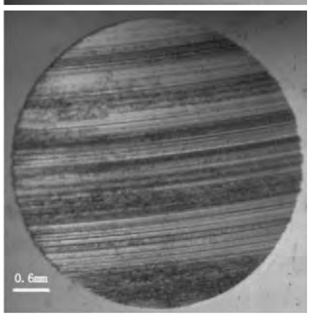
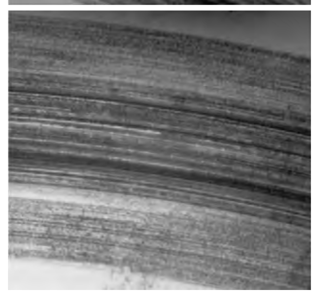
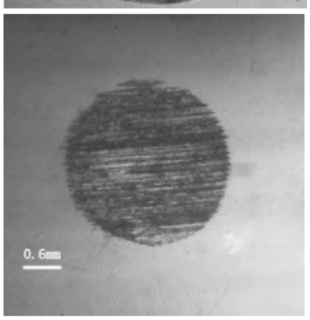
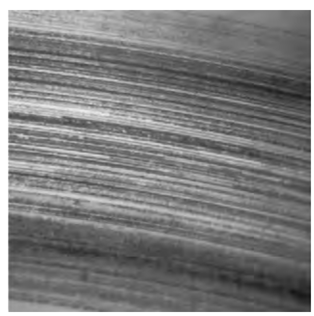
DMF (vol%)	Image of stationary ball	Image of rotating ball	AWSD (mm)	Roughness of rotational ball, R_a (μm)
0			0.443 ± 0.015	0.086 ± 0.01
2			0.427 ± 0.012	0.081 ± 0.015
4			0.370 ± 0.01	0.047 ± 0.014
6			0.40 ± 0.01	0.061 ± 0.01
8			0.440 ± 0.02	0.072 ± 0.01

Table 3 (*continued*)

DMF (vol%)	Image of stationary ball	Image of rotating ball	AWSD (mm)	Roughness of rotational ball, R_a (μm)
10			0.477 ± 0.015	0.081 ± 0.012
20			0.503 ± 0.015	0.093 ± 0.015
100			0.297 ± 0.021	0.045 ± 0.013

[18]. The four-ball test can be used to evaluate the tribological behaviour of both oils and fuels. For example, it can be used to determine the wear behaviour of hydraulic pump components or for comparing the differences between new and used engines oils including the effect of particulate contamination on the lubricating properties of the used oils. Such tests have been shown to correlate well with both bench and general vehicle field tests [19,20]. In addition, the four-ball tribometer is commonly utilised for assessing the lubrication properties of oils in China because the method is fast, simple and cheap compared to the HFRR and SLBOCLE methods [21].

In this study, the lubrication properties of DMF were evaluated using an MQ-800 four-ball tribometer. The base gasoline, DMF and the effect of DMF concentration on the lubrication properties of gasoline/DMF blends of 2, 4, 6, 8, 10 and 20 vol% were all examined. The effect of DMF concentration on the lubrication properties of gasoline/DMF blends was also examined. A schematic of the four-ball tribometer is shown in Fig. 1. In this study, two different properties were tested: friction and wear. For the lubricity tests, the load and rotational speed were set at 100 N and 500 rpm, respectively. The tests were conducted at a humidity of 55% for 30 min at an ambient temperature (approximately 25 °C) to minimise fuel evaporation. This ensured that the remaining fuel in the specimen holder was enough to cover the test specimens. The extreme pressure performance (PB value) was measured at 1760 rpm for 10 s according to the ASTM D2783 standard. The friction coefficient and the wear scar diameter (WSD) were obtained according to the Penn State Sequential Test Method [18]. The average wear scar diameter WSD of the three lower balls was measured using an optical microscope. Tests were repeated three times and the average value was used to evaluate the wear properties. Surface roughness measurement system (Taylor–Hobson-6) was used to measure the surface roughness (R_a) of the worn zone with a magnification of 10,000 times.

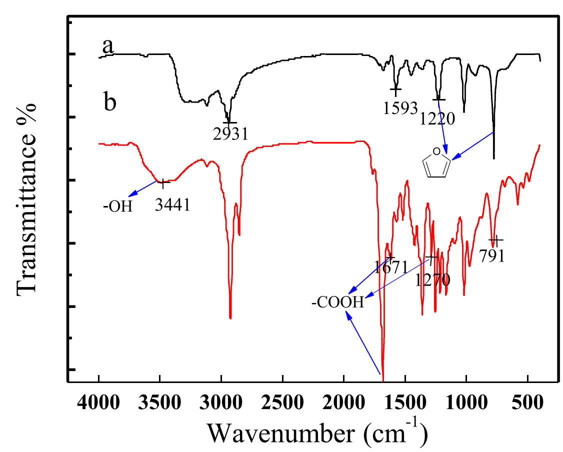


Fig. 5. FT-IR spectra of DMF before and after friction. a: before friction, b: after friction.

Fourier transform infrared spectroscopy (FT–IR) was used to analyse the composition structures of the DMF before and after tribological testing. Total ion current (TIC) of DMF before and after testing was analysed by GC–MS (GCT type), and the mass spectrometer was set to scan for molecular masses ranging from 10–1000, using selective ion monitoring modes. The FT–IR (Nicolet 67 type of cell, spectrum-100, resolution 0.09 cm^{-1}) was produced by the Perkin Elmer Inc., Waltham, MA, USA and the GCT GC–MS was manufactured by Micromass UK Ltd. in Manchester, UK.

3. Results and discussion

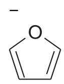
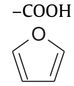
3.1. Frictional properties

The average friction coefficients of DMF and gasoline were 0.038 and 0.089 respectively, confirming that DMF has better lubricity than gasoline. Fig. 2 shows that the friction coefficients of both gasoline and DMF increased slowly with time. Under certain conditions, the friction coefficient increased with applied load which could increase the contact area [21]. In this paper, it was found that the friction coefficient increased with prolonged time, perhaps as a result of increase in the contact area. Fig. 3 shows the variation of the average friction coefficient of the gasoline with the increasing blend volumes of DMF. It was found that DMF greatly enhanced the antifriction properties of gasoline at all selected concentrations. The average friction coefficients were 0.064, 0.062, 0.050, 0.048, 0.041 and 0.041 for the respective volumes of DMF to gasoline (to 20 vol%); Fig. 3 also indicates that saturation occurs around 10 vol% with no further improvements in friction reduction with the increasing DMF concentration.

3.2. Wear resistance

The AWSD variation for gasoline with the increasing DMF content is shown in Fig. 4. The AWSDs are taken from the three stationary test specimens. It was found that the antiwear properties of gasoline with DMF were significantly improved with increasing DMF content when less than 4 vol%. The AWSD of gasoline was 0.443 ± 0.015 mm, while the AWSD of the gasoline with 4 vol% DMF was 0.37 ± 0.01 mm, a decrease of 16%. AWSD increased significantly with the increasing volumes of DMF above 4 vol%. The decline in the antiwear properties of DMF in the blends greater than 4 vol% may be due to excessive amounts of DMF causing negative effects on the process of friction. An alternative explanation could be attributed to the amount of DMF involved in the chemical reactions that occur during the friction process. Moreover, when the amount of the DMF was more than the counterbalance of the adsorption on the friction surface, the antiwear properties of gasoline were reduced. It can be concluded that the decrease in friction coefficient of DMF in gasoline outweighs that of the wear resistance.

Table 4
The wave number corresponding to the main groups of DMF before and after friction.

Conditions Wave number (cm^{-1})	Before friction Corresponding to groups	After friction Corresponding to groups
3441	–	–OH (hydroxyl)
2931, 2850	$-CH_3$	$-CH_3$, $-CH_2$
1750,	–	–COO–
1671		C=O
1593	C=C	–
1270	–	–COOH
1220, 791		

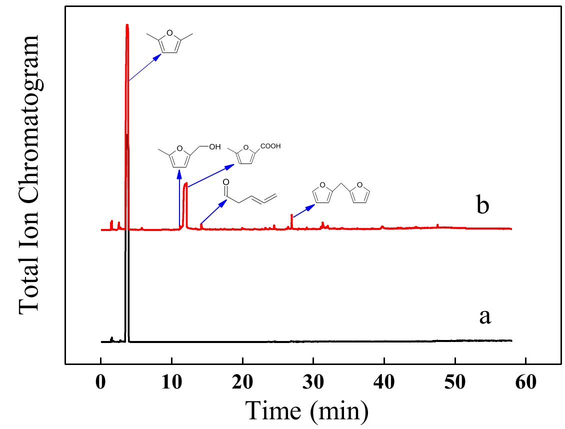


Fig. 6. GC–MS chromatograms of DMF before and after friction. a: before friction, b: after friction.

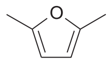
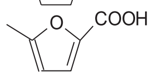
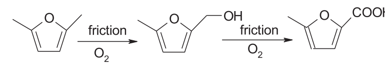
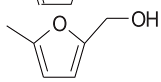
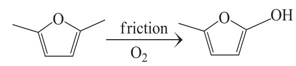
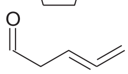
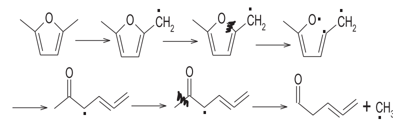
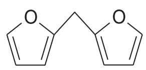
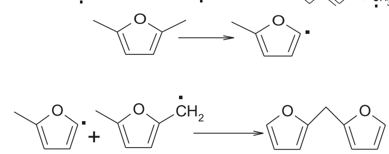
3.3. Surface analysis

Table 3 shows the variation of AWSD and images of the worn surfaces of the steel test specimens lubricated by gasoline blended with DMF under the described experimental conditions. When lubricated by DMF, the characteristic wear scars of the test specimens are thin and slim. Conversely the specimens lubricated by gasoline displayed wider and deeper wear scars. This confirms that DMF has better wear resistance than gasoline. The amount of active functional groups such as the carboxyl (–COOH) are different in DMF and gasoline, perhaps explaining the difference in wear resistance and the topography of the subsequent surface damage. These active functional groups could react with the iron (Fe) elements inside the steel specimens to produce a robust antiwear film during the rubbing period. Table 2 shows DMF has a higher viscosity than gasoline which indicates that DMF has good adsorption on the rubbing surfaces during the friction process [22–24]. Table 2 also shows that the acid value of DMF was higher than that of gasoline, indicating that DMF had a higher free fatty acid (FFA) content. From a molecular prospective, pure DMF does not contain FFAs. The presence of FFA in this instance may be a result of the differing preparation and storage methods used for the test fuels. FFAs can enhance the lubricity of engine fuels, although the influence is minimal [14].

3.4. Structure analysis

Fig. 5 and Table 4 present the FT–IR spectra of the base DMF before and after testing. The peaks have been assigned as follows: (i) 3441 cm^{-1} is the hydroxyl group (–OH) flex vibration peak, which is a wide peak and shifts to the low wave number because of the hydrogen association effect; (ii) both 2931 cm^{-1} and 2850 cm^{-1} are the methyl group ($-CH_3$) and methylene group ($-CH_2$) flex vibration peaks; (iii) 1671 cm^{-1} is ascribed to the carbonyl group (–C=O), which shifts to the low wave number because of the conjugate effect of the hydroxyl group (–OH); (iv) 1593 cm^{-1} is ascribed to the double carbonyl group (C=C); (v) 1270 cm^{-1} is ascribed to the carboxyl group (–COOH); (vi) 1220 cm^{-1} is ascribed to the furan group. From the absorption peaks (i) to (vi), it can be concluded that there are alcohol, carboxylic acid, carbonyl and furan groups in DMF after testing, offering a fundamental interpretation of the tribological properties of DMF. The detailed components are confirmed by the GC–MS results shown in Fig. 6.

Table 5
Main chemical components in DMF and relative reactions.

No.	Retained time (min)	Structure formula	Height before friction (%)	Height after friction (%)	Relative reaction [10]
1	1.57	CH_3OH	0.47	1.12	–
2	3.67		99.65	92.79	–
3	11.16		0	0.33	
4	12.07		0	4.51	
5	14.11		0	0.6	
6	26.86		0	1.61	

The TIC of the distilled fractions shown in Fig. 6 and Table 4 describes the variation of chemical compounds in DMF before and after friction. They show that friction has induced a series of new chemical compounds. These compound changes were consistent with the results of FT–IR, as shown in Fig. 5. The hydroxyl and carboxyl groups existed in the DMF after friction which could allow an interpretation to why adding a certain concentration of DMF to gasoline promotes antifriction properties. Deterioration of the anti-frictional properties of the fuel blends occurred above blends fractions of 4 vol%.

The tribological process, with a number of frictional products such as alcohols, acids and furans, is highly complex. At present, there are few studies on the components of DMF after frictional testing. In our paper, it is possible to conclude that there are alcohols, acids and furans in the gasoline/DMF blends after friction. Moreover, it is difficult to clarify the reactions of DMF during the frictional process. However, the main products of DMF after lubricity testing can be expressed by the reactions reported in Ref. [10] and in Table 5. The occurrences of hydroxyl and carboxyl groups in the main products of DMF after lubricity testing can be regarded as the friction-induced chemical reactions between rubbing pairs and DMF.

4. Conclusions

1) The friction reduction of pure DMF (2,5-dimethylfuran) is superior to that of gasoline. As for the blend of DMF and gasoline, the friction reduction of blends was improved with the DMF content. At the same time, the friction reduction of blends became stable and similar with pure DMF when the blend volume fraction of DMF in gasoline is more than 10 vol%.
2) In case of wear resistance the pure DMF also shows a better performance than that of gasoline. However there is striking phenomenon for the blend volume fraction of DMF and gasoline. The wear resistance increased with DMF content in the blend up to 4 vol%. The wear resistance decreased with DMF content in the blends as DMF increased above 4 vol%, as the chemical composition after testing was shown to change. Nevertheless, pure DMF indicated the best wear resistance.
3) Vol% DMF in gasoline was shown to be the optimal ratio for reducing friction and improving wear resistance.
4) The occurrences of hydroxyl and carboxyl groups in the main products of DMF after lubricity testing can be regarded as friction-induced chemical reactions between rubbing pairs and DMF.

Acknowledgements

The authors wish to express their thanks to Ms. Y.Y. Shi and Mr. M. Tian for their assistance in the experimental work. The financial support from the National Natural Science Foundation of China (Grant no. 50875071), National High Technology Research and Development Program of China (863 Program) (Grant no. 2012AA051803) and the EPSRC project (Grant no. EP/F061692/1) are also gratefully acknowledged.

References

[1] Encinar JM, González JF, Rodríguez-Reinares A. Ethanolysis of used frying oil. Biodiesel preparation and characterization. Fuel Process Technology 2007;88: 513–22.
[2] Ribeiro NM, Pinto AC, Quintella CM, Da Rocha GO, Teixeira LSG. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. Energy Fuels 2007;21:2433–45.
[3] Bhale BV, Deshpande NV, Thombre SB. Improving the low temperature properties of biodiesel fuel. Renewable Energy 2009;34:794–800.
[4] Sendzikiene E, Makareviciene V, Janulis P. Oxidation stability of biodiesel fuel produced from fatty wastes. Polish Journal of Environmental Studies 2005;14: 335–9.
[5] Takeshita EV, Rezende RVP, Guelli SMA, De Souza U, Ulson de Souza AA. Influence of solvent addition on the physicochemical properties of Brazilian gasoline. Fuel 2008;87:2168–77.
[6] Luque R, Herrero-Davila L, Campelo JM, Clark JH, Hidalgo JM, Luna D, et al. Biofuels: a technological perspective. Energy and Environmental Science 2008;1:513–96.
[7] Román-Leshkov Y, Barrett CJ, Liu ZY, Dumesic JA. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. Nature 2007;447:982–5.
[8] Zhao HB, Holladay JE, Brown H, Zhang ZC. Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural. Science 2007;316: 1597–600.
[9] Grela MA, Amorebieta VT, Colussi AJ. Very low pressure pyrolysis of furan, 2-methytfuran, and 2,5-dimethylfuran. The stability of the furan ring. Journal of Physical Chemistry 1985;89:38–41.
[10] Wu XS, Huang ZH, Yuan T, Wei LX. Identification of combustion intermediates in a low-pressure premixed laminar 2,5-dimethylfuran/oxygen/argon flame with tunable synchrotron photoionization. Combustion and Flame 2009;156:1365–76.

[11] Zhong SH, Turner D, Zhang J, Xu HM, Wyszynski ML. An innovative biofuel approach—2,5-Dimethylfuran (DMF): combustion performance and emissions in a GDI engine. SAE paper no. 2009-01-2824.
[12] Margaroni D. Fuel lubricity. Industrial Lubrication and Tribology 1998;50(3): 108–18.
[13] Wei DP. Study on the lubricity of gasoline fuels I. A preliminary investigation on the lubricity of European gasoline fuels. ACTC Petrolei Sinica (Petroleum Process Section) 2000;16:7–12 [in Chinese].
[14] Hu JB, Du ZX, Li CX, Min EZ. Study on the lubrication properties of biodiesel as fuel lubricity enhancers. Fuel 2005;84:1601–6.
[15] Wadumesthrige K, Ara M, Salley SO, Ng KYS. Investigation of lubricity characteristics of biodiesel in petroleum and synthetic fuel. Energy Fuels 2009;23:2229–34.
[16] Knothe G, Steidley KR. Lubricity of components of biodiesel and petrodiesel. The origin of biodiesel lubricity. Energy Fuels 2005;19:1192–200.
[17] Westbrook SR. Survey of low sulfur diesel fuels and aviation kerosenes from US Military Installation, SAE paper no. 952369.
[18] Wain KS, Perez JM, Chapman E. Alternative and low sulfur fuel options: boundary lubrication performance and potential problems. Tribology International 2005;38:313–9.
[19] Perez J, Hansen R, Klaus E. Comparative evaluation of several hydraulic fluids in operational equipment, a full-scale pump stand test and the four-ball wear tester. Part II. Phosphate esters, glycols and mineral oils. Lubrication Engineering 1989;46:249–55.
[20] Perez J, Klaus E, Hansen R. Comparative evaluation of several hydraulic fluids in operational equipment, a full-scale pump stand test and the four-ball wear tester. Part III. New and used hydraulic fluids. Lubrication Engineering 1995;5:416–22.
[21] Wang QJ, Xu YF, Hu XG, Zhu XF. Experimental study on friction and wear characteristics of bio-oil. Transactions of the Chinese Society of Agricultural Engineering 2008;24:188–92 [in Chinese].
[22] Kajdas C, Majzner M. Boundary lubrication of low-sulphur diesel fuel in the presence of fatty acids. Lubrication Science 2001;14(1):83–108.
[23] Knothe G, Steidley KR. Kinematic viscosity of biodiesel fuel components and related compounds. Influence of compound structure and comparison to petrodiesel fuel components. Fuel 2005;84:1059–65.
[24] Muñoz M, Moreno F, Monné C, Morea J, Terradillos J. Biodiesel improves lubricity of new low sulphur diesel fuels. Renewable Energy 2011;36: 2918–24.