Reduction of Persistent Organic Pollutant Emissions during Incinerator Start-up by Using Crude Waste Cooking Oil as an Alternative Fuel

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ABSTRACT

Illegal harvesting and recycling of waste cooking oil, also referred to as "gutter oil" in many countries, poses a great food safety threat. Thus, in this study the feasibility of using waste cooking oil as an auxiliary fuel in the furnace of laboratory waste incinerator was evaluated in terms of toxic pollutant emissions. Two fuel blends (W20D80 and W40D60) were blended from varying proportions of diesel fuel (D100), and waste cooking oil (W100) and their physio-chemical characteristics were subsequently determined and compared. Thermogravimetry analysis (TGA) and derivative thermogravimetry (DTG) of D100, W100, W20D80 and W40D60 showed that diesel fuel consist of more volatile short aliphatic hydrocarbons, while the waste cooking oil and its blends had more thermal stable unsaturated long chain molecules. After the *de novo* synthesis window of 200–400°C, 40% of waste cooking oil and 60% of diesel (W40D60) was injected at around 500–700°C, and reduced the toxicity concentrations of PCDD/Fs and PCBs by an average of 86% and 94%, respectively. This study demonstrated that, by using waste cooking oil as a fuel blend, not only can reduce the possibility of "gutter oil" being put in the food to damage the health of human beings, but also can be recycled as a kind of green fuel to reduce the emissions of persistent organic pollutants (POPs).

Keywords: PCDD/Fs; PCBs; Waste cooking oil; Laboratory waste incinerator; Auxiliary fuel.

INTRODUCTION

Frying food in fast food chains, restaurants, homes, cafeterias and even street food vendors has been shown to generate large quantities of waste cooking oil (Fajriutami *et al.*, 2013). Estimated amounts of waste cooking oil from developed countries are about $4.0–6.0 \times 10^6$ tons year^{-1} in Japan (Yu *et al.*, 2002; Ramadhas *et al.*, 2004), 1.35×10^5 tons year^{-1} in Canada, $7.0 \times 10^5–1.0 \times 10^6$ tons year^{-1} from EU countries, and 2.0×10^5 tons year^{-1} from UK (Chhetri *et al.*, 2008), 4.5×10^6 tons year^{-1} in China, 5.0×10^5 tons year^{-1} in Malaysia (Kalam *et al.*, 2011) and 7.0×10^4 tons year^{-1} from Taiwan (Tsai *et al.*, 2007). After many frying cycles at elevated temperatures and, while exposed to the atmosphere, the waste oil deteriorates in quality in comparison to the original fresh oil making, thus rendered unsuitable for further use and consumption. During the transition from original fresh to waste cooking oil, many transformations occur, which include thickening and becoming viscous, change in color from yellow to brown, formation of foam, and increase in specific heat (Maskan, 2003; Kulkarni and Dalai, 2006; Hassanien and Sharoba, 2014).

Therefore, in order to prevent potential environmental and health problems such as clogging of drainage systems, river pollution (Yu *et al.*, 2002), illegal selling after refining (Liang *et al.*, 2013) and possible introduction of toxic compounds in the food chain (Kulkarni and Dalai, 2006; Lu and Wu, 2014), many nations have set up policies to ban illegal disposal of waste cooking oil (Kalam *et al.*, 2011; Patil *et al.*, 2012). New ways of tapping into waste cooking oil as an economic resource have been researched over the years (Valdés and Garcia, 2006; Naima and Liazid, 2013). Application of waste cooking oils include soap making, biodiesel production, co-combustion in diesel engines, furnaces and burners (Ramadhas *et al.*, 2004; Zheng *et al.*, 2006; Lu *et al.*, 2013; Chang *et al.*, 2014a; Mahfouz *et al.*, 2015; Tsai *et al.*, 2015a, b, 2016) due to the relatively low cost of waste cooking oil as a raw material (Sabudak and

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Yildiz, 2010). Conversely, waste cooking oil contains large amounts of free fatty acids (FFA), high water content and impurities, which are major drawbacks in soap making and biodiesel production (Leung and Guo, 2006; Predojević, 2008; Sabudak and Yildiz, 2010), while high viscosity values poses problems in pumping and injection in diesel engines (Kalam *et al.*, 2011; Mwangi *et al.*, 2015). Additionally, the high cost of biodiesel production from raw waste cooking oil presents an obstacle to successfully exploit it as a resource.

Therefore, raw waste cooking oil has been directly used as a cheap substitute for conventional petroleum fuels in combustion process (Kalam *et al.*, 2011; Mwangi *et al.*, 2015). Kalam *et al.* (2011) noted that application of 5% waste palm oil and 5% waste coconut oil mixed with 95% diesel fuel in an engine resulted in reductions of the emissions of unburned hydrocarbon (HC) (17–23%), smoke (1.75–3.33%), CO (7.3–21%), and NOx (1%), when compared to diesel fuel operation. However, Yu *et al.* (2002) utilized waste cooking oil to run diesel engine without modification, but reported increased emissions of CO, NO and SO_2 compared to diesel fuel. Similarly, Mahfouz *et al.* (2015) used it in swirl burners with preheating to avoid clogging in the nozzles and reported higher HC and CO_2 emissions compared to diesel fuel. Waste cooking oil can also be used to reduce polycyclic aromatic hydrocarbons from mobile and stationary sources (Cheruiyot *et al.*, 2015; Mwangi *et al.*, 2015).

Start-up procedures have been shown to be significant and important periods in terms of PCDD/F emissions during incinerator operations (Tejima *et al.*, 2007; Wang *et al.*, 2007; Karademir and Korucu, 2013; Lin *et al.*, 2014). According to Wang *et al.* (2007) and Karademir and Korucu (2013), the PCDD/F emissions during start-up procedures could be 2–4 times higher than those of the whole year normal operations (Cheruiyot *et al.*, 2016). The elevated PCDD/F emissions during start-up procedures of incinerators have been attributed to incomplete combustion of diesel and feeding wastes, state of cleaning of boiler section as well as furnace temperature passing through PCDD/F formation window inevitably (Wang *et al.*, 2007). Consequently, high PCDD/F emission during start up procedure will result in *de novo* based memory effect, that is, the surfaces of the boiler and pipe are contaminated by soot particles containing high PCDD/F contents as well as hydrocarbons, which improve PCDD/F formation via *de novo* synthesis of at these locations (Li *et al.*, 2011).

The aim of this study was to determine the feasibility of using waste cooking oil as an auxiliary fuel in the incinerators furnace during start-up procedure, because waste cooking oil contains much lower aromatic hydrocarbon contents, which were important precursors of PCDD/Fs and PCBs. The appropriate mixing proportions of the waste cooking oil and diesel fuel were evaluated based on the reduction on the emissions of PCDD/Fs and PCBs during start-up procedure.

EXPERIMENTAL SECTION

Preparation of Various Fuel Blends for Candidate Test Fuels Used in Start-up Procedure

Four kinds of fuels/oils were investigated in this study,

including neat diesel fuel (D100) (CPC Corporation, Taiwan), neat/virgin cooking oil (F100) and waste cooking oil (W100). From the three kinds of base fuels/oils, two blends; waste cooking oil blended with 80% diesel fuel (W20D80), and W40D60, were prepared by blending the base fuels at various proportions by volume basis.

Stability tests of the blends were done by centrifugation at 5000 rpm for 15 minutes and observed for cloudiness and separation of layers. The flash point was done using a Pensky–Martens closed cup method, while the IKA C500 automated bomb calorimeter was used to determine the calorific values of the fuel blends.

A SUNTEX SP-701 pH meter was used to ascertain the pH values, while the viscosity of resulting blends were obtained using a Brookfield DV-I+ viscometer apparatus. Measurement of acid values was done using AT-510 N automatic titrator. To determine the specific gravity of the blends the simple method of volumetric-weight determination was employed.

The ash content in the blend was quantified by heating the fuel samples in a high temperature furnace at 800°C for three hours and obtaining the difference in the weight from after and before heating. An infrared moisture analyzer was used to determine the moisture content in each of the blends. The combustibles were computed using the following relationship: combustibles % = 100% – (water content + ash content) %.

The elemental analysis was carried out using Elementar Analyzer to give the content of nitrogen (N), carbon (C), hydrogen (H), sulphur (S) and the oxygen (O) content was calculated as follows:

$$O_2 = 100\% - (N + C + H + S)\% \qquad (1)$$

On the other hand, thermogravimetry analyses (TGA) were done using a Perkin Elmer Pyris Diamond Thermogravimetry Analyzer. Air (21% O_2 and 79% N_2) was chosen to simulate actual combustion conditions. The flow rate of air was held constant at 100 mL min^{-1}. The heating was non-isothermal and approximately 10 mg of fuel blends were heated from room temperature (30°C) to 850°C at a rate of 10°C per minute.

Test Fuels Used in Start-up procedure

Out of the five types of fuels tabulated in Table 2, only 3 fuel blends were chosen for the consecutive studies on start-up of the incinerator. These included D100, W20D80 and W40D60. The emissions of PCDD/Fs and PCBs were treated as the base scenario for comparison, when D100, the original fuel for this incinerator, was used. On the other hand, W20D80 and W40D60 were selected in order to study the influence of higher fractions of raw waste cooking oil on PCDD/F emissions during co-combustion in the incinerator furnace.

Sampling Strategy

The characteristics and operating conditions of the laboratory waste incinerator in this research are outlined in Table 1. Previously, the flow diagram of incinerator and air

Table 1. Characteristics of the Laboratory Waste Incinerator.

Item	Laboratory waste incinerator
Treatment process	Two combustion chamber (primary and secondary)
Wastes	Laboratory waste and intermediates (ashes and sludge)
composition	Approximately Organic (67%) and inorganic (33%)
APCD	Two cooling tower, bag filter and wet scrubber
Primary chamber	Operation at 850°C
Secondary chamber	Operation at 1050°C
Two cooling towers	Flue gas temperature from 1050°C to 180°C
Activated carbon injection	Injected prior to bag filters to remove PCDD/Fs
Bag filters	To remove particulates (120°C–180°C)
Wet scrubber (Packing tower)	Remove acid and cooling (180°C–80°C)

pollution control devices has been well outlined elsewhere (Wu *et al.*, 2014). As shown in Fig. 1, the stack flue gas samplings for PCDD/Fs and PCBs were conducted at four furnace temperature regimes designated as A (25–200°C), B (200–400°C), C (580–750°C) and D (850–900°C) during start-up procedure of a laboratory waste incinerator for D100, W20D80 and W40D60.

For all the three fuel trials, D100 was the only fuel combusted, when the furnace temperatures were below 550°C. This is because the flash point and viscosity of waste cooking oil are higher than those of diesel fuel, and it was found that injecting waste cooking oil blends at temperature range around 500°C could sufficiently improve and enhance flow characteristics, resulting in more complete combustion based on some preliminary tests and thermogravimetry (TGA) results.

Temperature regime A was chosen to represent PCDD/F concentrations before furnace temperature passed through PCDD/F formation window, while temperature regime B, which was around 200–400°C, represented PCDD/F concentrations resulted from *de novo* synthesis. Temperature regimes C (580–750°C) and D (850–900°C) were chosen to evaluate the impact of using waste cooking oil-based diesel blends as auxiliary fuels on the emission of PCDD/Fs and

PCBs. Temperature regime D (850–900°C) is also the operational temperature when the waste starts to feed into furnace.

Stack Flue Gas Samplings and PCDD/Fs and PCBs Analyses

The stack flue gas samples were collected isokinetically following U.S. EPA Modified Method 23 using a U.S. EPA Modified Method 5 sampling train. The sampled flue gas volumes were normalized to the dry condition of 760 mmHg and 273 K, and denoted as Nm^3.

The quartz fiber filter and XAD-2 from each sampling were combined to represent the whole stack flue gas sample. Internal standards were spiked into the samples before Soxhlet extraction with toluene, and were used to monitor the extraction and cleanup procedures. After the sample was extracted in a Soxhlet extractor with toluene for 24 hours, the extracts were concentrated, and then treated with concentrated sulfuric acid, and this was followed by a series of sample cleanup and fractionation procedures, including a multi-layered silica column, alumina column and an activated carbon column. During the alumina column cleanup, non-planar PCBs were eluted with 15 mL hexane, and were then further eluted with 25 mL DCM/hexane (1/24, v/v) for
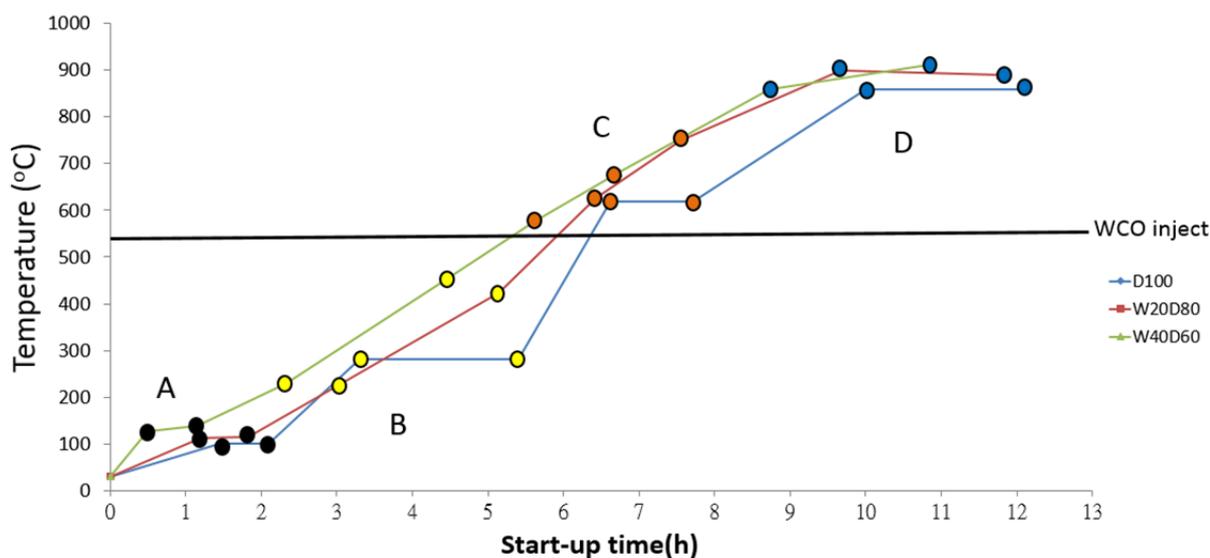

Fig. 1. Pollutant sampling and waste cooking oil injection points during furnace operation.

activated carbon column use. The activated carbon column was sequentially eluted with 5 mL toluene/methanol/ethyl acetate/hexane (1/1/2/16, v/v) for planar PCBs, which was further followed by 40 mL of toluene for PCDD/Fs. Before instrument analyses, the planar and non-planar PCBs eluates were mixed together, representing the PCB samples. The eluate was concentrated to approximately 1 mL and transferred to a vial. This was then further concentrated to near dryness using a stream of nitrogen. Immediately prior to injection, 10 μL of the standard solution for recovery checking was added to the sample extract to minimize the possibility of loss.

The solutions in the vials were then analyzed to identify seventeen 2,3,7,8-substituted PCDD/F and twelve dioxin-like PCB congeners using a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS). The detailed analytical procedures and instrumental analytical parameters of PCDD/Fs and PCBs, are presented in our previous works (Wang *et al.*, 2003; Wang *et al.*, 2010a; Wang *et al.*, 2010b).

Quality Assurance and Quality Control

At preliminary stages of sampling, the XAD-2 resin was spiked with PCDD/F surrogate standards pre-labeled with isotopes such as $^{37}Cl_4$-2,3,7,8-TCDD, $^{13}C_{12}$-1,2,3,4,7,8-HxCDD, $^{13}C_{12}$-2,3,4,7,8-PeCDF, $^{13}C_{12}$-1,2,3,4,7,8-HxCDF and $^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF. The recorded recoveries of PCDD/F surrogate standards were in the range of 93%–118% which met the recovery criteria of U.S. EPA Modified Methods 23 (70%–130%). In an addition, the recoveries of precision and recovery (PAR) and internal labeled standards all met the relevant standards. More over to ensure minimal contamination from sampling and analytical processes, the field and laboratory blanks were carried for each batch of sampling and analyses. The total amounts of PCDD/Fs in the field and laboratory blanks were less than 0.1% of the actual stack flue gas samples while for the PCBs, the blanks were below the detection limits.

RESULTS AND DISCUSSION

Physiochemical Properties of Fuel Blends

Table 2 shows the characteristics of various fuels including heavy oil from waste cooking oil (W100) fresh cooking oil (F100) and neat diesel fuel (D100) as well as blends of waste cooking oil and diesel fuel. Comparing the properties of fresh cooing oil (F100) and waste cooking oil (W100) it is evident that frying or use of high heat during cooking resulted in increased specific gravity, heating value, acid value, pH and water content but decreased flash point. The increase was about 2%, 220%, 2%, 11%, 300% and 200% for specific gravity, ash content, heating value, pH, acid value and water content, respectively.

Similarly, Fajriutami *et al.* (2013) noted that cooking process caused a rise in density, acid value and FFA content in waste cooking oil including viscosity increase, specific heat increase, surface tension increase, and color change compared to raw soybean oil. The increase in FFA is due to higher rate of hydrolysis tri-glycerides in presence of water and heat conditions (Sabudak and Yildiz, 2010). Another study by Predojević (2008) investigated the properties of waste cooking oil and reported values for specific gravity, which were similar to this study (0.92–0.936), while the acid value in that study was ranged between 1.86 and 3.31 (mg KOH g^{-1}), which is lower than that of the current study (7.47 mg KOH g^{-1}).

Table 2. Physio-Chemical Properties of Fuel Blends used in this study.

	D100	F100	W100	W20D80	W40D60
Fuel Physio-Chemical Properties					
Specific gravity	0.850	0.946	0.961	0.872	0.900
Flash point (°C)	75.0	314	244	79.0	83.0
Ash content (%)	< 0.01	0.0250	0.0810	0.0300	0.0500
Heating value(kcal kg^{-1})	10,400	9,030	9,200	10,200	9,960
pH	7.50	5.70	6.30	7.20	7.00
Acid value (mg KOH g^{-1})	~0	1.91	7.47	1.49	3.00
Water content (%)	< 0.05	~0	2.00	0.400	0.800
Stability				OK	OK
Water and residue (%)	< 0.05	~0	~0	~0	~0
Combustibles content (%)	> 99%	~100	99.9	> 99%	> 99%
Elemental Analysis					
N (%)	0.550	0.245	0.665	0.573	0.600
C (%)	85.0	73.5	76.1	83.2	81.4
H (%)	13.5	10.9	11.3	13.0	12.6
S (%)	< 0.0002	0.0160	0.0465	0.00930	0.0200
O (%)	1.02	15.4	11.9	3.20	5.38
Chlorine content and aromatics content in WCO and diesel					
Cl (ppm)	0.33[a]		5.48	1.36[b]	2.39[b]
Aromatics (%)	27.1[a]		< 0.01	< 0.01[b]	< 0.01[b]

[a] Chang *et al.*, 2014a.
[b] determined by mass balance.

For comparison, the aromatic and the chlorine contents in the diesel and waste cooking oil were determined. The chlorine content in the waste cooking oil (5.48 ppm) was approximately 17 times that in the neat diesel fuel (0.33 ppm), while the aromatic content in the diesel fuel (27.1%), was approximately 2700 times than in the waste cooking oil (0.01%). The chlorine content in the waste cooking oil biodiesel was about 5 times that of diesel fuel (1.5 ppm) in the previous research (Chang *et al.*, 2014a), while the aromatic content was the same as the current study. By using mass balance the chlorine content in both W20D80 and W40D60 were 1.36 and 2.39 ppm, respectively.

From Table 2, it is evident that compared to all other fuel blends, the properties of both W20D80 and W40D60 were very close to those of diesel fuel (D100). These include specific gravity, ash content, heating value, water content and combustible content. The flashpoints of W20D80 and W40D60 were slightly higher than those of diesel fuel but much lower compared to other fuel blends that were initially investigated in the preliminary tests. This comparability between W20D80 and W40D60 and diesel fuel made them the best choices for study.

Effect of Temperature on Viscosity

Fig. 2 shows the relationships between viscosity and temperature for waste cooking oil and diesel blends. Determination of viscosity as a rheological parameter is important considering the pumping process of fuel blends from one vessel to another such as storage tank to the furnace (Fasina *et al.*, 2006). At room temperature (25°C), the viscosity of waste cooking oil (48 cP) was about 6 times that of diesel fuel (8 cP) in this study. In their study, Phan and Phan (2008) pointed out that the viscosity of waste cooking oil was approximately 10 to 15 times that of diesel fuel possibly due to the presence of higher molecular glycerides (Esteban *et al.*, 2012). Valdés and Garcia (2006) proposed that after heat treatment presence of functional groups with stronger long range dipole-dipole attractions may be responsible for thicker waste cooking oils. The viscosities of the W20D80 and W40D60 were lower than

that of W100 but still larger than that of D100. The viscosity of W20D80 and W40D60 decreased with increasing diesel fractions and at higher temperatures the viscosity of waste cooking oil fuel blends was close to that of D100 compared to that of W100.

Overall, for the fuels, the viscosity decreases with increasing temperature as a result of increased thermo-movement resulting from weakened intermolecular forces and increased flow (Santos *et al.*, 2005). Other rheological studies have confirmed this behavior on edible vegetable oils (Maskan, 2003; Fasina *et al.*, 2006; Kim *et al.*, 2010; Hassanien and Sharoba, 2014). This temperature dependence of viscosity of oils has been shown to be advantageous in application of vegetable oils in diesel engines to reduce wear and engine aging (Esteban *et al.*, 2012).

TGA and DTG

The Figs. 3(A), 3(B) and 3(C) show the trends of thermogravimetric analysis and derivative thermogravimetric analysis of D100, W20D80 and W40D60, respectively. Thermogravimetric analysis is a characterization techniques used to ascertain thermal stability and decomposition behavior of fuels and biomass at various temperature regimes and different atmospheres (Bagoria *et al.*, 2012; Dwivedi and Sharma, 2016). Thermogravimetric analysis simply evaluates the variation in weight of a fuel sample occurring as a result of physical or chemical change versus either time or temperature. Physical changes may include sublimation, evaporation and/or condensation, while chemical changes may involve degradation, decomposition and/or oxidation. The first derivative of the thermogravimetry, the DTG curve, highlights the occurrence of a mass loss or mass gain event and indicates the specific temperature range, where a particular decomposition reaction occurs.

The TGA and DTG results of the D100 show that the main combustion zone was around 200°C corresponding to the highest peak on the DTG curve and steepest slope on the TGA curve. This corresponded to degradation of volatiles in the diesel fuel via volatilization. On the other hand, the fuel blends of W20D80 had minor peaks between 350 and
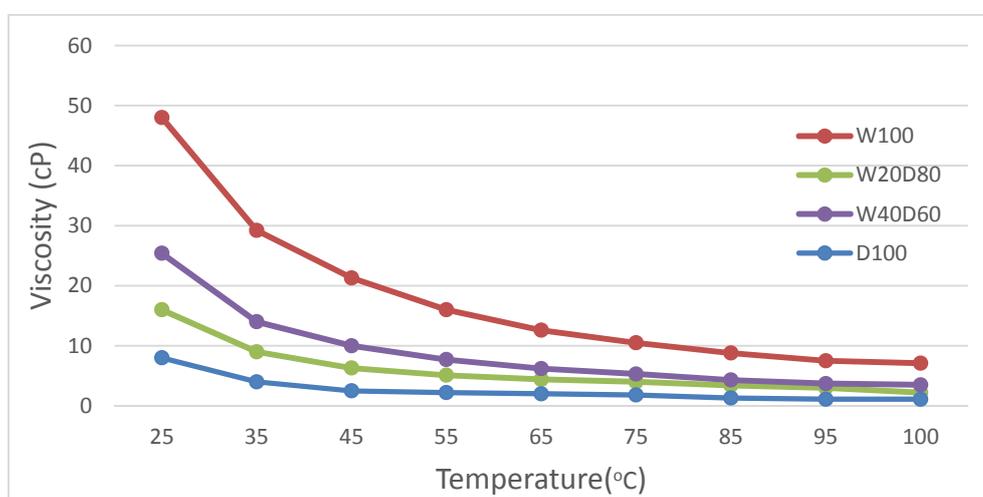

Fig. 2. Impact of temperature on the viscosity of various fuel blends.
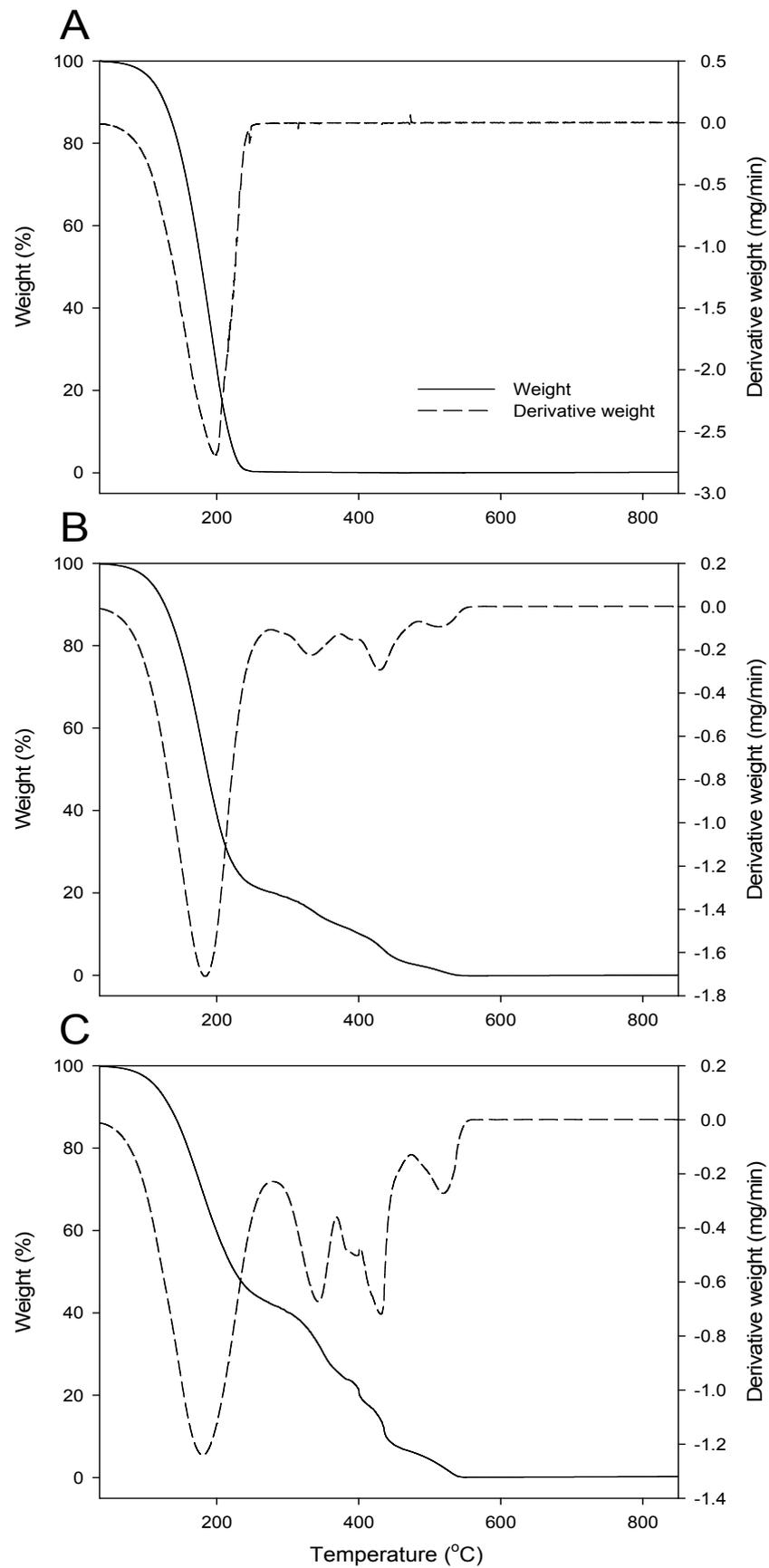
Fig. 3. The TGA and DTG diagram of different blending ratio of waste cooking oil (A = D100, B = W20D80, C = W40D60).

550°C in addition to the major peak at 200°C. The peaks in the W40D60 were more pronounced compared to those of W20D80. The first peak for W20D80 and W40D60 signifies degradation of diesel components, while the peaks appearing between 350°C and 550°C show degradation of waste cooking oil components. The intensity of DTG peaks for W40D60 was greater due to higher waste cooking oil fractions and shows four distinct degradation's phases corresponding to four peaks on the DTG curve.

According to Santos *et al.* (2004), the peaks falling between 380–480°C is due to degradation of monosaturated fatty acids whereby double bonds are broken, while that between 480–600°C corresponds to saturated fatty acids decompositions. Diesel mainly consists of short chain hydrocarbons such as aliphatic hydrocarbons with carbon chains ranging between C_{10} and C_{25} (Schauer *et al.*, 1999), which are easily volatilized at lower temperatures. On the other hand, waste cooking oil contains large molecular hydrocarbons, polymerized derivatives of esters and high amount of free fatty acids (FFA) (Ho *et al.*, 2014). The fatty acids include linoleic, oleic, palmitic and stearic (Fajriutami *et al.*, 2013), which are decomposed at higher temperatures due to longer carbon chains and presence of the thermally stable unsaturated bonds. In their study, Felizardo *et al.* (2006) reported that waste cooking oils contained C16:0, C18:0, C18:1, C18:2, C18:3, C20:0 in terms of 8.29–8.65%, 4.02–4.70%, 27.3–30.6%, 55.1–57.6%, 0.30–2.28%, and 0.55–0.65% by mass respectively. Additionally, Leung and Guo (2006) noted that waste cooking oil may contain C20:1, C22:0, C22:1, and C24:0 in amounts less than 0.05% by mass.

For both the diesel and waste cooking oil, thermal degradation is endothermic considering the shape of the DTG curves (Chen and Kuo, 2011). This observation is similar to the behavior exhibited by biodiesel from sunflower, castor, and soybean seeds (Silva *et al.*, 2011) as well as grape, peanut, olive and palm seeds (Cursaru and Mihai, 2013).

Emission Levels and Trends of PCDD/Fs and PCBs for Fuel Blends at Different Operation Stages

The Table 3 shows the mass and toxicity concentrations of PCDD/Fs and PCBs for D100, W20D80 and W40D60 at various sampling times designated A, B, C and D. As seen in the Table 3, the TEQ of D100 increased as the temperature rose from room temperature to about 500–700°C and further increase the range above 850°C. As for PCDD/Fs, the highest amount was emitted at sampling time A for W20D80 (2.73 ng Nm^{-3}) as well as the corresponding toxicity concentrations (0.343 ng WHO-TEQ Nm^{-3}), which were increased by 14 and 23 times, respectively, compared to those of diesel fuel (0.193 ng Nm^{-3} and 0.015 ng WHO-TEQ Nm^{-3}) at the same period. Similarly, for PCBs, the highest mass and toxicity concentrations were 14.8 ng Nm^{-3} and 0.0210 ng WHO-TEQ Nm^{-3}, respectively, both observed at sampling period A for W20D80 corresponding to an increase of 73% and 106% in relation to those of diesel fuel for the same sampling time. On the other hand, for W40D60 the only increase was observed for PCDD/Fs (by 23%) in terms of mass concentrations, while the toxicity concentrations of dioxins and PCBs were reduced by factors of 19% and 74%, respectively.

A review by McKay (2002) suggests that dioxin formation in combustion processes generally depend on the operating conditions such as temperature and oxygen levels/content (Yang *et al.*, 2015). Other factors include characteristics of input material including the aromatic and chlorine content (Preto *et al.*, 2005; Shibamoto *et al.*, 2007) in both fuels and feed/raw materials. Therefore, it is worth to note that diesel was used during the first test run and in the second test run diesel was used up to a temperature of 500–700°C and thereafter W20D80 was injected. Therefore, we can postulate that the increase of PCDD/Fs and PCBs observed in the second test with W20D80 at stage A, is mainly due to memory effect. Wu *et al.* (2014) described occurrence of memory effect at start up whereby as temperatures increase there is occurrence of desorption and release of PCDD/Fs or products of incomplete combustion, which result in elevated PCDD/Fs levels, which are carried away by flue gases. In the case of W40D60, which was used after the test run with W20D80, the levels of PCDD/Fs and PCBs reduced in terms of toxicity concentrations during the stage A sampling. This is because after using the W20D80

Table 3. Concentrations of PCDD/Fs and PCBs from incinerator fueled with waste cooking oil blends.

	Sampling period	A	B	C	D
PCDD/Fs					
D100	Mass (ng Nm^{-3})	0.193	1.49	0.751	1.14
	WHO-TEQ (ng WHO-TEQ Nm^{-3})	0.0150	0.0417	0.0746	0.129
W20D80	Mass (ng Nm^{-3})	2.73	0.523	0.733	0.454
	WHO-TEQ (ng WHO-TEQ Nm^{-3})	0.343	0.0473	0.0793	0.0504
W40D60	Mass (ng Nm^{-3})	0.237	0.254	0.202	0.154
	WHO-TEQ (ng WHO-TEQ Nm^{-3})	0.0122	0.0120	0.0139	0.0126
PCBs					
D100	Mass (ng Nm^{-3})	8.57	5.35	12.8	8.75
	WHO-TEQ (ng WHO-TEQ Nm^{-3})	0.0102	0.0132	0.0416	0.0565
W20D80	Mass (ng Nm^{-3})	14.8	1.57	3.52	2.21
	WHO-TEQ (ng WHO-TEQ Nm^{-3})	0.0210	0.00301	0.00778	0.00696
W40D60	Mass (ng Nm^{-3})	1.86	0.565	1.07	1.26
	WHO-TEQ (ng WHO-TEQ Nm^{-3})	0.00265	0.00154	0.00256	0.00328

in the second test run, the emission characteristics and fingerprint of PCDD/Fs and PCBs were changed resulting in reduced memory effect.

More importantly is the emissions characteristics at sampling stages C and D, which corresponds to the periods during and after injection time of biodiesel blends, respectively. In comparison to the performance by diesel fuel, the addition of W20D80 caused reduction in the mass concentration by 2.4–60% and 73–75% for both PCDD/Fs and PCBs, respectively. The reductions in toxicity concentrations were averaging at 27% and 84%, for PCDD/Fs and PCBs, respectively. After addition of W40D60 the mass concentrations of PCDD/Fs and PCBs were reduced by approximately 73–85% and 86–92%, respectively, compared to diesel fuel at same conditions. The toxicity concentrations were reduced by about 81–90% and 94% for PCDD/Fs and PCBs, respectively.

Fig. 4 clearly shows the trends of the emitted levels of PCDD/Fs and PCBs for different operation times when using D100, W20D80 and W40D60, respectively. According to Fig. 4, when operating with diesel fuel, the emission rate and emission levels of both PCDD/Fs and PCBs are lowest at startup and increase gradually with increasing operation time. Considering W20D80, in Fig. 4, there is reduction in the emission rates in the first hour and the time between the second and third hour and further reduction in emission rates between the third and fifth hour. There is 44% and 45% reduction in emission rates of PCDD/Fs and PCBs,

respectively, when comparing periods between first and second hour and that between second and third hour. The consequent reduction when considering the time between second and third hour and third and fifth hour is approximately by 80% and 75% for PCDD/Fs and PCBs respectively. In Fig. 4, the emission rates for trend for PCDD/Fs in case of W40D60 rises steadily as time progresses, while that of PCBs initially reduces then increases gradually with operation time.

A closer look at values of emissions for stages C and D in the Table 3 and also Fig. 4 shows three distinct trends for different fuels which may show a correlation to the difference in fuel properties. Oxygen content serves to enhance the destruction of PCDD/Fs (Altwicker *et al.*, 1990). The oxygen contents in W20D80 (3.2%) and W40D40 (5.38%) were 3 and 5 times that in diesel fuel (1.02%). Thus, the reduction observed at operation periods falling between second and fifth hour for both W20D80 and W40D60 could be due to the dominating effect of destruction driven by oxygen content in the waste cooking oil. Chang *et al.* (2014a) attributed reduction of PCDD/F and PCB emission when using waste cooking oil biodiesel to possible complete combustion and reduction in aromatic contents in comparison to diesel fuel. Shaub and Tsang (1983) proposed that molecular oxygen in fuel may react with products of reaction between OH radical and aromatic compounds leading to ring opening which inhibits dioxin formation. Furthermore, W20D80 and W40D60 contain lower aromatic content and higher flash
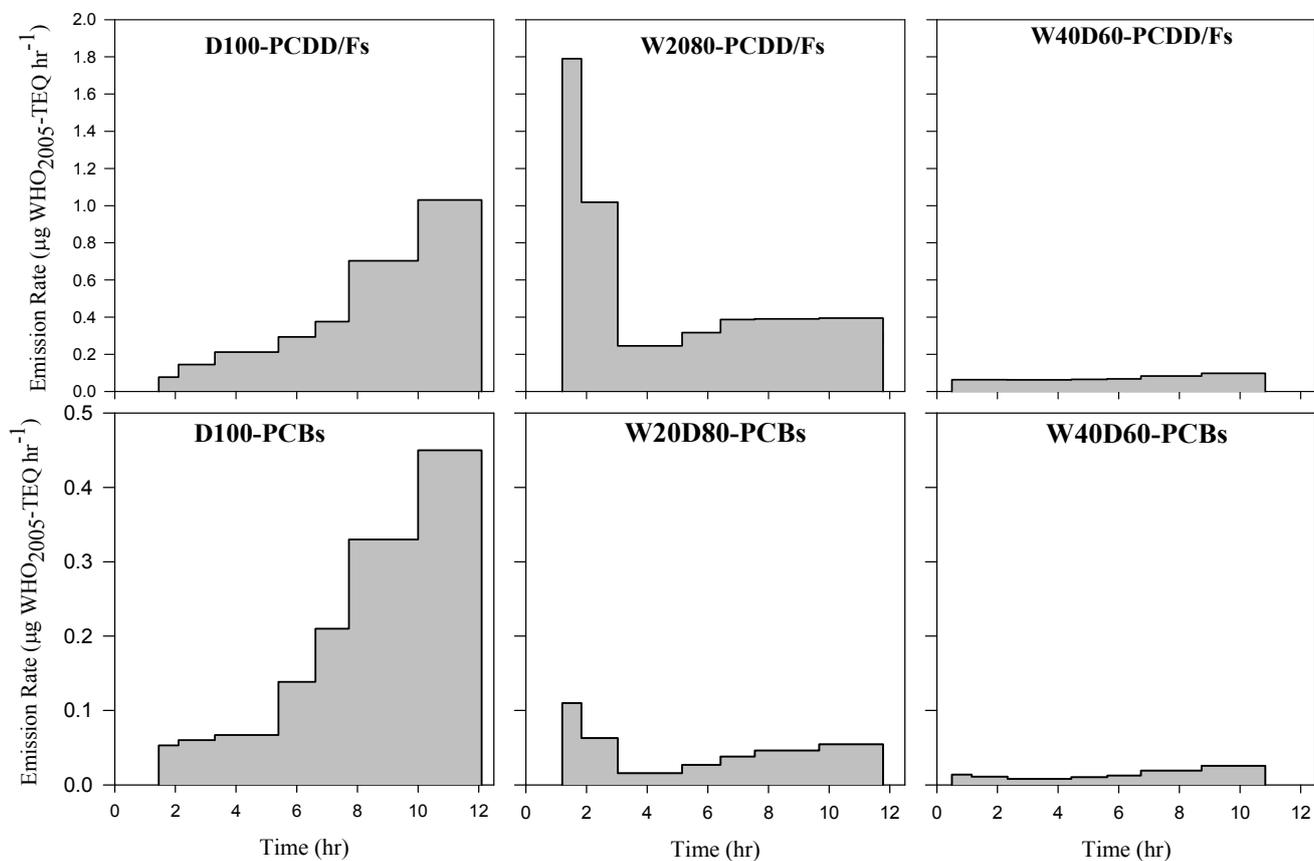

Fig. 4. Emission rates vs. time for PCDD/Fs and PCBs, respectively.

point as well as higher water content seen in Table 2 may have an inhibitory effect on dioxin formation.

Congener Profiles for Both Mass and Toxicity Fractions for PCDDFs and PCBs

The Figs. 5 and 6 show the dominant congeners in terms of mass concentrations and toxicity concentrations, respectively. For all the fuel and sampling times, the most abundant PCDD/F congeners were the highly chlorinated congeners including OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF

and 1,2,3,4,6,7,8-HpCDD in that order. The fractions were in the range of 8.5–35%, 2.5–19%, 10–17% and 6–19% for OCDD, OCDF, 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,7,8-HpCDD, respectively. Similarly, Chang *et al.* (2014a) identified OCDD, OCDF and ,2,3,4,6,7,8-HpCDD as dominant congeners in the diesel exhaust of an engine operated with waste cooking oil biodiesel while OCDD, OCDF and 1,2,3,4,6,7,8-HpCDF were the major mass contributors in vegetation, ambient air and soil samples in Taiwan (Kuo *et al.*, 2015).
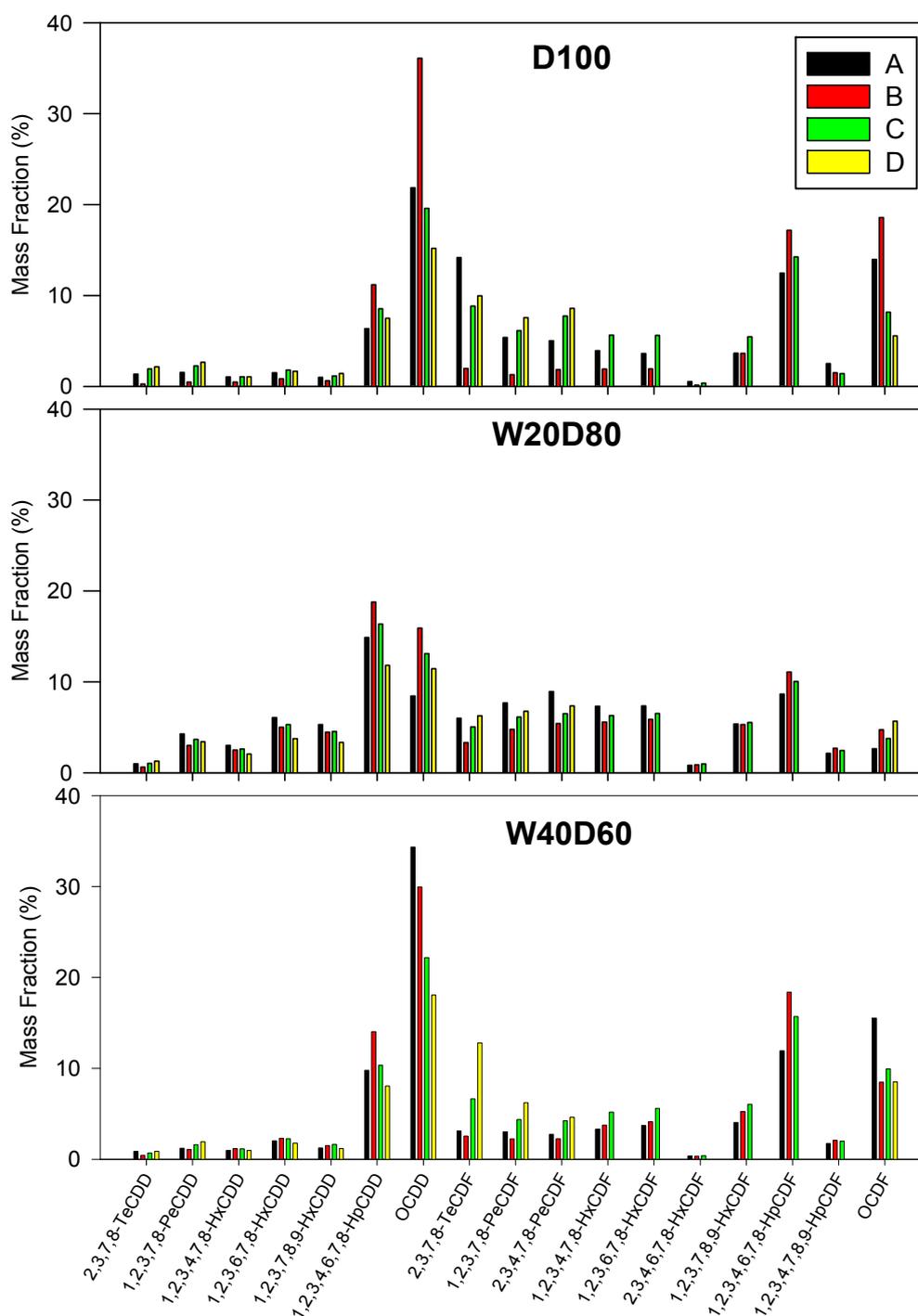

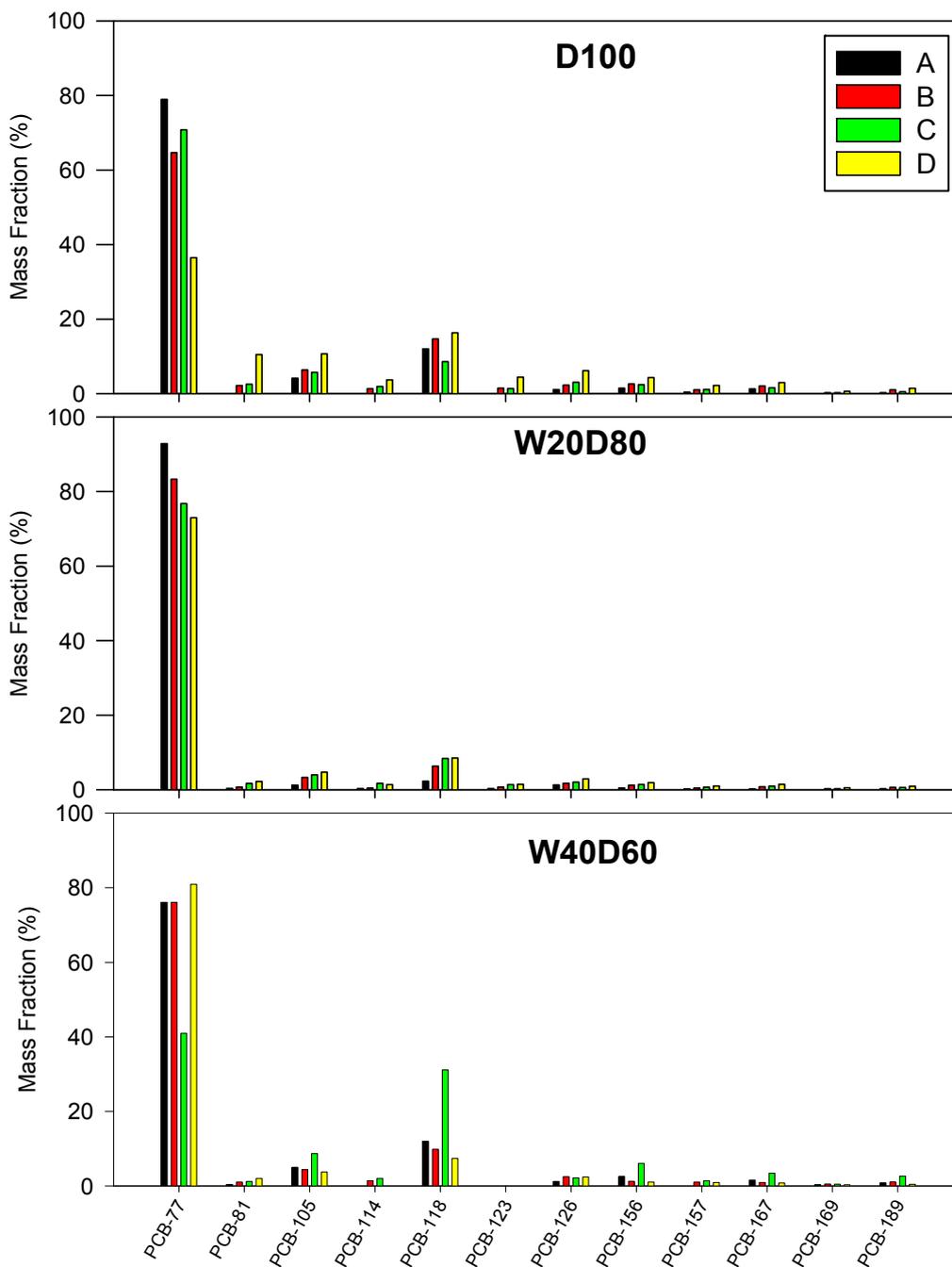**Fig. 5(a).** Congener Profiles for PCDD/F Mass Fractions.

Fig. 5(b). Congener Profiles for PCB Mass Fractions.

As for the PCBs, the dominant congeners in terms of mass fractions were the PCB-77 (40–80%) and PCB-118 (10–40%), which are usually the dominant congeners from the combustion sources. In Fig. 5(b) the fractions of PCB-77 has a clear decreasing trend with time or stage of sampling especially for W20D80 and more or less for D100. In the same figure the application of W40D60 diminished the fractions of PCB-77 and increased that of PCB-118 compared to D100 and W20D80. These congeners might be ubiquitous in nature considering they were recently identified as the main contributions to mass of PCBs in the soil, lichen and ornithogenic soils as well as penguins of Antarctica (Mwangi

et al., 2016). Previously, PCB-77 and PCB-118 have also been identified in diesel exhaust (Chang *et al.*, 2014a, b), river sediments (Toan, 2014), atmosphere of biomass burning sites (Chang *et al.*, 2013), vegetation, ambient air and soil samples (Kuo *et al.*, 2015).

The toxicity profiles in Fig. 6(a) show that the dominant congers are the lower chlorinated congeners such as 1,2,3,7,8-PeCDD (16–34%), 2,3,4,7,8-PeCDF (14–23%), 2,3,7,8-TeCDD (7–19%), and 2,3,7,8-TeCDF (4–18%) for PCDD/Fs. Fig. 6(b) indicates that the dominant PCB congener as PCB126 (86–96%), which shows conspicuous increasing with increasing time and temperature.
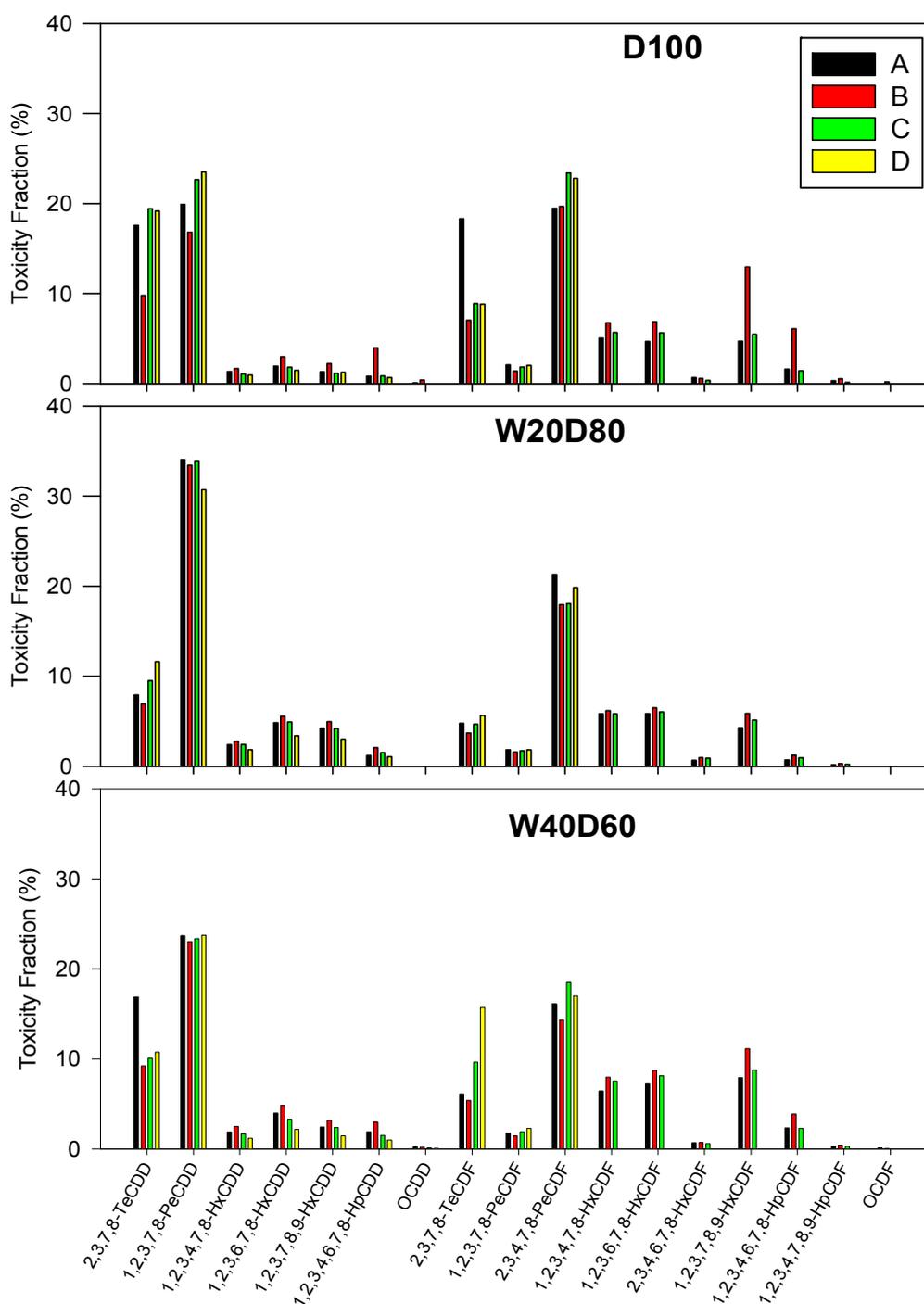
Fig. 6(a). Congener Profiles for PCDD/F Toxicity Fractions.

CONCLUSIONS

This study evaluates the impact of using waste cooking oil as an auxiliary fuel in the furnace laboratory waste incinerator. The waste cooking oil has a lower aromatic content but a higher chlorine and oxygen content compared to petroleum diesel. The results show that, in comparison to using diesel fuel, the application of waste cooking oil can inhibit PCDD/F formation resulting in toxicity reduction by an average of 26% and 86% when using W20D80 and

W40D60, respectively. Similarly, application of W20D80 and W40 D60 in the incinerator furnaces reduces the toxicity emissions of PCBs by factors of approximately 84% and 94%, respectively. In terms of performance, W40D60 resulted in greater reductions of toxic pollutant emissions compared to W20D80. The results of this study provide a useful way for both recycling of waste cooking oil as a kind of green fuel and reduction of persistent organic compound emissions in the waste incineration.
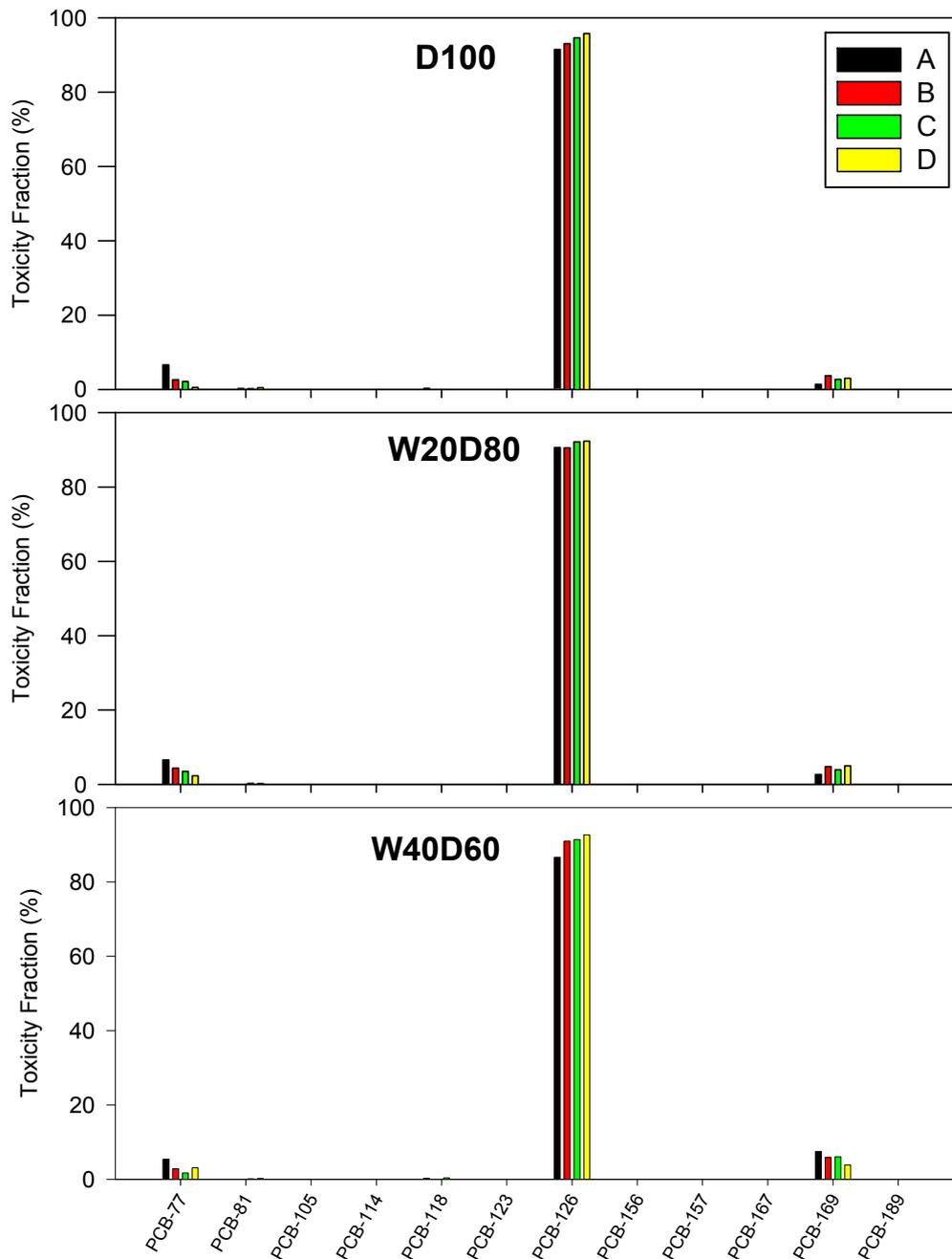
Fig. 6(b). Congener Profiles for PCB Toxicity Fractions.

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