



Effect of hydrogenation of palm oil products spiked with octachlorodibenzo-p-dioxin on dioxin congener profiles and toxic equivalent levels

Wilma Taverne-Veldhuizen^a, Ron Hoogenboom^b, Guillaume ten Dam^{b,1}, Rik Herbes^c, Vincenzo Fogliano^a, Pieter Luning^{a,*}

^a Wageningen UR, Food Quality and Design, Bornse Weiland 9, 6708, WG, Wageningen, the Netherlands

^b Wageningen Food Safety Research, Akkermaalsbos 2, 6708, WB, Wageningen, the Netherlands

^c Nederlandse Voedsel en Warenautoriteit, Catharijnesingel 59, 3511, GG, Utrecht, the Netherlands

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ABSTRACT

Between 1999 and 2020, there were twelve rapid alerts on dioxins in palm fatty acid distillate (PFAD) products, six of which were associated with hydrogenated palm fatty acid distillates (HPFADs). In palm oil refineries for food and feed, refined palm oil and PFADs can be processed into hydrogenated palm oil and HPFADs. This study investigated the effect of hydrogenation of palm oil products which contain OCDD and impact on the profiles of dioxins in palm oil products and on the toxic equivalent (TEQ) level. Palm oil and PFADs were spiked with octachlorodibenzo-p-dioxin (OCDD) and hydrogenated at different pressures, temperatures, and catalyst conditions. Initially, the concentrations of the lower-chlorinated dioxin congeners, some with a higher toxic equivalency factor, increased. Consequently, the TEQ levels increased and exceeded the regulatory limit. However, further hydrogenation extended the dechlorination of dioxins resulting in decreased TEQ levels. Optimisation of the hydrogenation process is required to reduce the risk of exceeding the limits on dioxins.

1. Introduction

Control of chemical hazards is vital in the food and feed industry to ensure safe products. Chemical hazards consist of applied, accidental, and background chemicals. Dioxins (polychlorinated dibenzo-p-dioxins and dibenzofurans, PCDD/Fs) and dioxin-like polychlorinated biphenyls (DL-PCBs) are well-known chemicals present at background levels in the environment and food chain (Ropkins, Ferguson, & Beck, 2003).

Dioxins have been involved in several food and feed safety issues, and have been reported regularly to the European (EU) Rapid Alert System for Food and Feed (RASFF) in the last few decades (Directorate-General for Health&Consumers, 2011, 2012, p. 48). Incidents (Directorate-General for Health&Consumers, 2011) with potential significant impact on consumers are e.g. the elevated PCDD/Fs and DL-PCBs in feed fat in Belgium in 1999, and too high PCDD/F levels in pork in Ireland in 2008 (Covaci et al., 2008; Heres, Hoogenboom, Herbes, Traag, & Urlings, 2010; Hoogenboom, Traag, Fernandes, &

Rose, 2015; RASFF, 2020; Traag, Kan, Van der Weg, Onstenk, & Hoogenboom, 2006). An incident with much lower levels occurred in Germany in 2011, where fatty acids intended for deinking, were used for feed production (Abraham et al., 2011). Nevertheless, this incident affected consumer trust and resulted in specific dioxin testing requirements for products derived from vegetable oils and blended fats (EC, 2012a, 2015), such as palm fatty acid distillates (PFADs), and hydrogenated palm fatty acid distillates (HPFADs). There were no rapid alerts related to crude and refined palm oil from 1999 to 2020. However, twelve notifications were related to exceeding the dioxin toxic equivalent (TEQ) level in PFAD products, and at least six of these were associated with HPFADs. The highest level in PFADs reported in the RASFF database was 2.3 ng WHO-TEQ/kg (RASFF, 2020), which justified the research on the mechanism of the chemical processes.

RASFF notifications indicate non-compliances and have an impact on the trust of consumers (Kher et al., 2013; TNS Opinion&Social, 2010, p. 78). Thus, the number of RASFF notifications in the oil and fat chain

* Corresponding author.

E-mail addresses: Wilma.Taverne@wur.nl (W. Taverne-Veldhuizen), Ron.Hoogenboom@wur.nl (R. Hoogenboom), Guillaume.ten.Dam@dpsystems.eu (G. Dam), Rik.herbes@nvwa.nl (R. Herbes), Vincenzo.Fogliano@wur.nl (V. Fogliano), Pieter.Luning@wur.nl (P. Luning).

¹ Present address Food Valley BTA12, Darwinstraat 7a, 6718 XR Ede, The Netherlands.

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must be reduced to protect the health of consumers and ensure their trust. RASFF notifications express the dioxin and DL-PCB levels in total TEQ, which is the sum of the calculated TEQ levels per congener. The individual TEQ level is calculated by multiplying the concentration with the toxic equivalency factor (TEF). These TEF values express the relative toxicity compared to the most toxic one, 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD), and were defined for 17 out of 210 congeners by the World Health Organization in 1998 and revised in 2005 (WHO₂₀₀₅-TEF) (Van den Berg et al., 2006). The maximum TEQ levels in food and feed were established by the EU Commission Regulations No 1259/2011 and No 277/2012 (EC, 2011; 2012b) based on the WHO-TEFs from 2005. However, RASFF only reports the TEQ levels to signal non-compliance of specific products, but they do not report the individual congener concentrations.

Dioxins consist of two interconnected benzene rings and can contain between one and eight chlorine atoms (De Greyt & Kellens, 2005; De Meulenaer, 2006). The 17 regulated PCDD/F congeners have four to eight chlorine atoms, always including the 2, 3, 7, and 8 positions, and the WHO₂₀₀₅-TEF values of these different congeners range between 0.0003 and 1. The highest-chlorinated octachlorodibenzo-p-dioxin (OCDD) and octachlorodibenzofuran (OCDF) congeners have the lowest WHO₂₀₀₅-TEF, which is 0.0003, whereas the lower-chlorinated TCDD and 1,2,3,7,8-pentachlorodibenzo-p-dioxin (PeCDD) have the highest WHO₂₀₀₅-TEF of 1 (De Meulenaer, 2006; Kulkarni, Crespo, & Afonso, 2008; Van den Berg et al., 2006). As a general principle, it is thought that these 17 congeners are poorly metabolized and as such accumulate in organisms, which may eventually result in levels causing adverse effects. Non-regulated congeners have no impact on the TEQ, e.g., 1,2,3,4-tetrachlorodibenzo-p-dioxin, which is a lower-chlorinated dioxin. However, the concentration of the non-regulated congeners can be important to elucidate the source of the contamination and more specifically in this study, to understand the impact of a process and the influence on the molecular structure.

Palm oil products, such as refined palm oil and PFAD, may be converted from (semi-)liquids to solids by hydrogenation. The unsaturated fatty acids become saturated in the presence of hydrogen and a catalyst. Previously, we reported that the main congener present in PFAD samples was OCDD (<limit of quantification (LOQ)–394 ng/kg, median 31.4 ng/kg), but this congener has a relatively low WHO₂₀₀₅-TEF (Taverne-Veldhuizen, Hoogenboom, Dam, Herbes, & Luning, 2020). The concentration of OCDD was slightly lower in the hydrogenated PFAD samples (<LOQ–345 ng/kg, median 24.5 ng/kg). However, the TEQ level (WHO₂₀₀₅-TEQ) was higher in these samples, suggesting that the hydrogenation affected the toxicity due to the replacement of chlorine atoms by hydrogen atoms. There are studies on the impact of hydrogenation on dioxins, but no studies have investigated whether the presence of OCDD in palm oil products during hydrogenation could increase the risk of exceeding the regulatory limits in products made thereof. Therefore, this study aimed to investigate the influence of the hydrogenation of palm oil products on regulated but also non-regulated (non-2,3,7,8-)PCDD/F congeners, and the impact on the total TEQ level.

2. Materials and methods

2.1. Design of experiments

Fig. 1 shows the industrial palm oil refining and hydrogenation, and the resulting palm oil products (refined palm oil, PFAD, hydrogenated palm oil, and HPFAD). We focused on the hydrogenation of refined palm oil (A) and PFAD (B).

The industrially produced refined palm oil and PFAD were hydrogenated at a pilot plant to investigate the effect of hydrogenation parameters on the fate of dioxins. The industrially produced refined palm oil (A) and PFAD (B) were therefore spiked with OCDD and OCDF, and the fate of the congeners during the hydrogenation was monitored. OCDD was chosen for the spiking test because it is the congener, that has

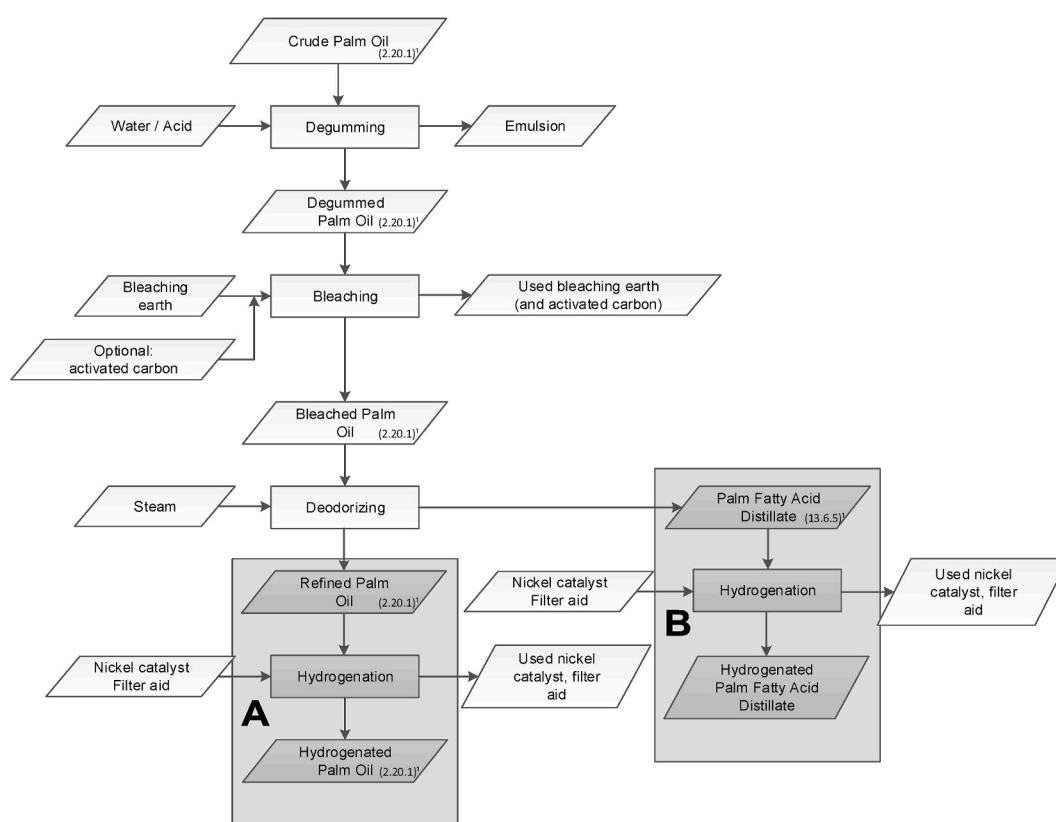


Fig. 1. Process flow diagram of palm refining and hydrogenation; (A) hydrogenation of palm oil and (B) hydrogenation of palm fatty acid distillate (PFAD).

a high occurrence in crude palm oil and palm oil fatty acid distillate (Taverne-Veldhuizen et al., 2020).

2.2. Spiking tests

2.2.1. Determining the hydrogenation conditions for the pilot plant

Prior to the pilot tests, the hydrogenation conditions were determined for achieving fully hydrogenated products. In routine practise, the process parameters of hydrogenation are adjusted to achieve a partially or fully hydrogenated product. This research aimed to achieve fully hydrogenated palm oil products. Therefore, the pilot plant conditions were first optimized to realise complete hydrogenation. For this the iodine value (IV), which reflects the saturation level of the fatty acids, was used to indicate the hydrogenation degree of the product. Higher saturation means lower IV and vice versa. The IV of fully hydrogenated palm oil products should drop from about 55 to below 10 (expressed in grams of I₂ per 100 g of fat). Pilot plant tests were performed to assess the relationship between the use of hydrogen and the IV and to assess when the product was fully hydrogenated. This test determined the impact of hydrogenation of palm fatty acid distillate on dioxin congeners without spiking (i.e. background analysis).

2.2.2. Actual spiking tests

In total four sets of tests were designed with different combinations of products, dioxin concentrations, and hydrogenation conditions. Table 1 shows the aim of each set, the concentration of the spiked congener, and the adjusted hydrogenation conditions in the pilot plant.

The first spiking tests aimed at determining the influence of hydrogenation on refined palm oil (A) and PFAD (B4) under similar catalyst and temperature conditions. In order to obtain hydrogenated palm oil and PFAD, the pressures were 2.5 and 30 bar, respectively. The second test aimed at comparing the influence of different temperatures, catalyst concentrations, and pressures on the hydrogenation of PFAD (B1–B4). The refined palm oil was not subjected to these tests because there were only RASFF notifications for HPFAD, which was therefore the main scope of this research. In the third spiking test, the behaviour of OCDF (B5) was measured and compared with the behaviour of OCDD (B2) under similar hydrogenation conditions. In the above three spiking tests, high concentrations of OCDD were spiked to determine their impact on the fate of dioxins. The fourth test was performed to verify the relevance of the spiking tests for OCDD levels observed in practice. In this test, the concentration of the spiked OCDD was 100 ng/kg based on previous monitoring data (Taverne-Veldhuizen et al., 2020), whereby the average OCDD concentration was 45 (ng/kg), and the standard deviation (51 ng/kg).

2.3. Spiking procedure

For the first test, 2.0 kg of refined palm oil (A) was spiked with 0.080 ml toluene with an OCDD concentration of 50.1 µg/ml (resulting in a

concentration of 2004 ng/kg refined palm oil). For the hydrogenation of PFAD codes B1 and B4, we added 0.100 ml toluene with OCDD 50.1 µg/ml to 2.5 kg PFAD. The calculated concentration was 2004 ng/kg. For the PFAD codes B2 and B3, 0.120 ml toluene with OCDD 50.1 µg/ml was added to 3.1 kg PFAD resulting in an OCDD concentration of 1939 ng/kg. For the PFAD code B5, the spiked concentration was 2024 ng/kg OCDF. For the PFAD code B6, 4 µl toluene with OCDD 50.1 µg/ml was added to 2007 kg PFAD resulting in a concentration of 99.85 ng/kg. For the addition of the toluene solution, the refined palm oil and PFAD were weighed in a vessel of 4 L. The vessel was put in the oven at 103 °C to ensure the fluidic condition of the raw material. Then, the vessel was placed on a heater under mechanical stirring at 65 °C. The toluene with OCDD or OCDF was added with a syringe. The mixture was kept under mechanical stirring for 2 h at 65 °C to ensure a homogenous solution.

2.4. Hydrogenation process

The spiked PFAD and refined palm oil were hydrogenated in a 2.5 L autoclave. The autoclave was under pressure of H₂, which was dropping because of the consumption of H₂ by the reaction. When necessary, i.e. the pressure dropped to about 2 bar, the reactor was refilled until the desired pressure. This procedure was repeated until there was no pressure drop. Re-filling was applied for code B1, B2 and B6. During the hydrogenation of refined palm oil, the pressure of the initial H₂ remained at 2.5 bar. For the hydrogenation of PFAD, the catalyst dosing was 0.3% or 2% of catalyst Pricat 9931 Ni, using 10 or 30 bar of initial H₂ pressure, at either 170 °C or 200 °C.

Samples were taken during the hydrogenation, and the time of sampling was recorded. The volume of each sample was 100 ml, which was stored using 100 ml brown sample glasses. The first sample of each test (t = 0) was taken when the target process settings were realised and the hydrogenation had started. When a sample was taken, 1.9 ml citric acid solution (50%) per kg product was added at 120–130 °C to stop the hydrogenation process. The hydrogenation time differed per test condition, because the IV was taken as a verification of total hydrogenation. Per test in 5 samples were taken spread over the total hydrogenation time.

2.5. Analysis of PCDD/Fs

Firstly, the level of the spiked OCDD was checked for the refined palm oil and PFAD products to test the validity of the congener analysis. Three accredited laboratories performed the analyses, based on gas chromatography/high-resolution mass spectrometry (GC/HRMS). The tests revealed recoveries of 65%, 96%, and 97%, as compared to the spiked level. The low recovery of 65% by one laboratory was most likely caused by the fact that the concentration loaded was beyond their calibration curve. This likely cause is also described in the literature (FVO, 2009; Oldenhof et al., 2011). Therefore, we selected only the two laboratories with 96% and 97% recoveries for further analyses. The

Table 1

Spiking tests with refined palm oil and PFAD to study the influence of hydrogenation on the fate of dioxin congeners.

Aim of the test	Code	Congener spiked	Spiked concentration (ng/kg)	Temperature (°C)	Catalyst (%)	Pressure (bar)
1. Determine the influence of hydrogenation on dioxins in refined palm oil (A) and PFAD* (B4) under similar catalyst and temperature conditions	A	OCDD	2004	200	2	2.5
	B4	OCDD	2004	200	2	30
2. Compare the influence of different catalyst concentrations, temperature, and pressure on dioxins in PFAD	B1	OCDD	2004	170	0.3	10
	B2	OCDD	1939	170	0.3	30
	B3	OCDD	1939	170	2	30
	B4	OCDD	2004	200	2	30
3. Compare the behaviour of OCDD and OCDF during hydrogenation	B2	OCDD	1939	170	0.3	30
	B5	OCDF	1939	170	0.3	30
4. Verify the relevance of the pilot tests and compare with monitoring results of commercial products	B6	OCDD	99.9	170	0.3	30

*Palm Fatty Acid Distillate.

**For comparison purposes B4 is used for test set 1 and 2, B2 is used for test set 2 and 3.

concentrations of the regulated dioxin congeners were analysed in both laboratories according to the EU Commission Regulation No 252/2012, laying down methods of sampling and analysis for the control of dioxin levels in certain foodstuffs. The national reference laboratory analysed both the regulated and the non-regulated congeners using a previously described procedure (Taverne-Veldhuizen et al., 2020).

3. Results and discussion

Before investigating the effect of hydrogenation on PFAD, the proper hydrogenation settings were assessed to confirm the right hydrogenation level. Iodine value was below 10 after 90 min of hydrogenation (appendix c). Moreover, measuring of the background congener concentration showed that the initial concentration of the regulated dioxins was 12.15 ng/kg and decreased to 0.05 ng/kg after 240 min of hydrogenation at 170 °C, 30 bar and 2% catalyst (appendix c).

3.1. Effect of hydrogenation of two different palm oil products on dioxin levels

The first test aimed to investigate the fate of hydrogenation on the behaviour of dioxins by spiking the congener OCDD in commercial refined palm oil and PFAD. Fig. 2 shows the changes in the profiles of dioxin congeners during the hydrogenation of refined palm oil (2a) and PFAD (2c), and the impact on the WHO₂₀₀₅-TEQ (2b and 2d). As mentioned above, not only the 17 regulated PCDD/Fs were analysed but also the levels of other non-2,3,7,8-congeners were estimated. These are represented by the dark and light green parts of the bars.

Fig. 2a shows that the total concentration of the dioxin congeners in refined palm oil decreased from 2015 ng/kg to 997 ng/kg within 15 min of hydrogenation and to 16 ng/kg after 75 min. The IV, which indicates the completion of the hydrogenation, declined from 58 to 2 within 75 min. This means that the refined oil was already fully hydrogenated. In this period, the concentration of the regulated octachlorodibenzo-p-dioxin (OCDD) (blue bar) decreased from 1987 ng/kg to 2 ng/kg, and the non-regulated congeners increased substantially (green bar).

The regulated dioxin congener 2,3,7,8-TCDD was not detected. The concentrations of other lower-chlorinated dioxin congeners, such as

1,2,3,7,8-PeCDD and HxCDDs and HpCDD, increased after 15 min and decreased after 75 min. The lower chlorinated and regulated congeners have a relatively high TEFs compared to OCDD. Fig. 2b shows the impact of these congeners on the WHO₂₀₀₅-TEQ level in the palm oil. After 15 min, the WHO₂₀₀₅-TEQ was around 3 ng WHO-TEQ/kg and exceeded the maximum level but was below the ML at later time points, at the end of the hydrogenation.

Fig. 2c shows that the total concentration of dioxin congeners in PFAD decreased from 1963 ng/kg to 976 ng/kg in 270 min. It also took 270 min before the IV dropped from 53 to 2, which is much longer than for the oil. The concentration of the OCDD decreased from 1493 ng/kg to 0.7 ng/kg. However, the concentrations of the regulated lower-chlorinated congeners 2,3,7,8-substituted HpCDD (yellow bar), HxCDDs (orange bar), and PeCDD (red bar) increased up to 180 min, but then decreased. Fig. 2d shows the impact of these changes on the WHO₂₀₀₅-TEQ level; after 15 min of hydrogenation, the maximum level was slightly exceeded, but a high value was observed at 180 min. After 270 min, at the end of the hydrogenation, the WHO₂₀₀₅-TEQ decreased but was still above the maximum level. As shown in Fig. 2c, the levels of the non-regulated congeners (green bars) increased over time, with a shift in the ratio between the higher (dark) and lower (light) chlorinated congeners towards the end.

The hydrogenation of refined palm oil and PFAD exhibited the same pattern (Fig. 2a–d); only the speed of dechlorination differed. Therefore, the likelihood of elevated TEQ levels in fully hydrogenated palm oil is lower than that in HPFAD. The findings of this study may elucidate why there have been no rapid alerts for hydrogenated palm oil in the EU RASFF database, whereas, there have been multiple alerts for hydrogenated PFAD (RASFF, 2020).

3.2. Effect of hydrogenation parameters on the hydrodechlorination rate of dioxins

Multiple process parameters (test B1, B2, B3 and B4 in Table 1) were further investigated to examine the fate of congeners during the hydrogenation of PFAD. Fig. 3 shows the changes in the concentrations of three selected dioxin congeners during the hydrogenation of PFAD with different process parameters and the impact on the TEQ level. The

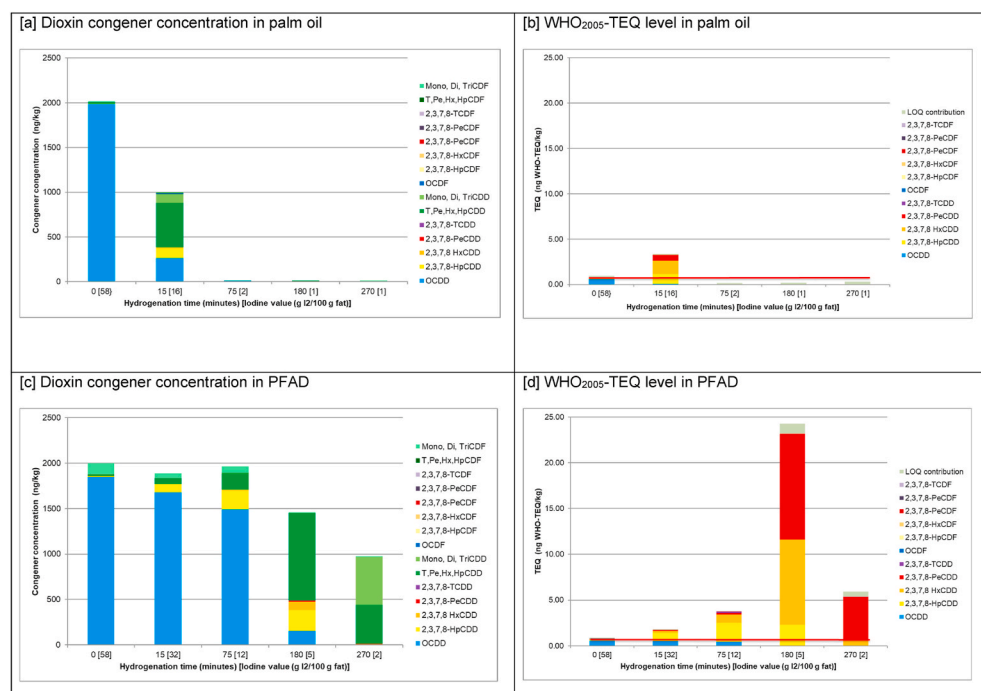


Fig. 2. Effect of hydrogenation of refined palm oil and palm fatty acid distillate (PFAD) on the levels of dioxin (Fig. 2a and c) and the toxic equivalents (WHO₂₀₀₅-TEQ) (Fig. 2b and d); the maximum regulatory level is indicated with the red line (see Fig. 2b and d). On the X-axis, the Iodine Value is shown between brackets as indication of the hydrogenation grade. * LOQ is limit of qualification. **T = Tetra, Pe = Penta, Hx = Hexa, Hp = Hepta, O = Octa. *** CDF = Chlorodibenzofuran, CDD = Chlorodibenzo-p-dioxin. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

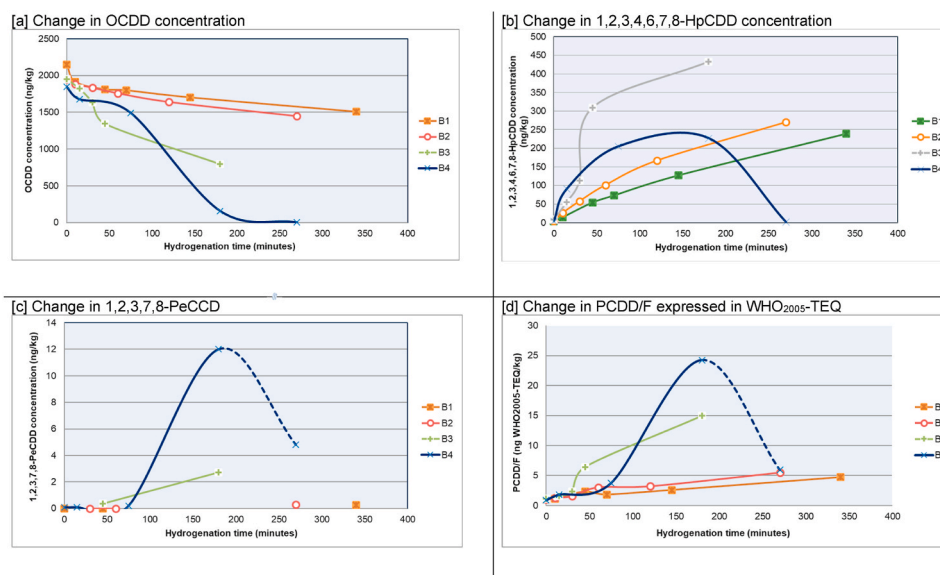


Fig. 3. Changes in the concentrations of OCDD (a), 1,2,3,4,6,7,8-HpCDD (b), and 1,2,3,7,8-PeCDD (c) during hydrogenation of palm fatty acid distillate and impact on WHO₂₀₀₅-TEQ levels (d); process parameters varied, 10 bar versus 30 bar (test B1 vs B2), 0.3% and 2% catalyst (B2 vs B3), 170 °C vs 200 °C (test B3 vs B4), respectively.

graphs of these selected dioxin congeners present the different effects of hydrogenation parameters. Overall, Fig. 3 indicates that higher pressure (B1 vs B2), catalyst concentration (B2 vs B3), and temperature (B3 vs B4) increased the dechlorination rate of OCDD (Fig. 3a) over time. Supplementary materials b2–5 show the measured concentrations of all other PCDD/F congeners. In all tests, the iodine value decreased below 10, which indicated full hydrogenation according to sector guidelines.

The test with the lowest temperature (170 °C), dose of the catalyst (0.3%), and pressure (10 bar) had the lowest dechlorination rate (Fig. 3, test B1). At the end of the hydrogenation, the corresponding TEQ value (4.41 ng WHO₂₀₀₅-TEQ/kg) was above the maximum level (0.75 ng WHO₂₀₀₅-TEQ/kg), as shown in Fig. 3d. An increase in the pressure (Fig. 3, test B2) from 10 bar to 30 bar (0.3% catalyst, 170 °C) resulted in a moderate reduction in the concentration of OCDD and the formation of lower-chlorinated congeners, in particular the 1,2,3,7,8-PeCDD (Fig. 3b and c). At the end of the hydrogenation, the corresponding TEQ (5.47 ng WHO₂₀₀₅-TEQ/kg) was slightly higher than observed in lower pressure.

The increase in the catalyst dose (from 0.3% to 2% at 30 bar and 170 °C) resulted in a lower concentration of OCDD at the end of the hydrogenation (Fig. 3, test B3). However, the concentrations of the regulated HpCDD (Fig. 3b, test B3), HxCDDs (supplementary material b), and PeCDD (Fig. 3c, test B3), as well as of the non-regulated congeners (supplementary material b) increased. The regulated lower-chlorinated congeners caused a substantial increase in the TEQ values, as shown in Fig. 3d, test B3. During the whole hydrogenation process, all the TEQ values exceeded the maximum level reaching the highest level (15 ng WHO₂₀₀₅-TEQ/kg) at 180 min.

Fig. 3 test B4 shows that the increase in temperature from 170 °C to 200 °C (at 30 bar and 2% catalyst) fully reduced OCDD (Fig. 3a, test B4). Furthermore, the concentration of the regulated HpCDD (Fig. 3b, test B4) firstly increased, but then disappeared at the end of the hydrogenation. The transformation of OCDD into the lower-chlorinated congeners (Fig. 3b and c) indicated that it was a dechlorination process rather than an adsorption process as previously suggested (Addison, Zinck, Ackman, & Sipos, 1978). The highest calculated TEQ level was at 180 min. The TEQ finally decreased; however, it remained above the maximum level at 240 min of hydrogenation (Fig. 3d, test B4). It is unknown if the concentration peaks at 180 min or later; the dotted line denotes the period 180–240 min.

The decrease in the TEQ level can be explained by the findings of

earlier studies. A previous study of Sajiki and co-authors (2002) demonstrated that the hydrogenation of PCBs with a Pd/C catalyst fully dechlorinated the PCBs into biphenyl (Sajiki, Kume, Hattori, Nagase, & Hirota, 2002). Ukisu and Miyadera (2004) investigated the dechlorination of the non-regulated 1,2,3,4-TCDD during hydrogenation and observed that the degree of dechlorination was dependent on the type of the used catalyst (Pd/C or Pd/Al₂O₃) (Ukisu & Miyadera, 2004). Moreover, in another study different types of catalysts for the dechlorination of PCBs were investigated. In this study Ni/C, Pd/C, and Ni–Pd/C proved to be good catalysts (B. Z. Wu et al., 2012). All these studies confirmed the mechanism of replacement of chlorine atoms by hydrogen atoms in the congeners using catalysts.

In the studies mentioned above, the researchers did not evaluate the impact of the chlorine replacement in the congeners on the risk of creating more toxic congeners and exceeding the regulatory limits for dioxins in hydrogenated fat products. Only Zhang and co-authors (2007) mentioned the potential risk of partial dechlorination in the introduction (Zhang, Chen, Zhang, Ni, & Liang, 2007).

3.3. Difference of dechlorination between OCDD and OCDF

The dechlorination of OCDF was compared with that of OCDD to identify possible differences in their fate (Fig. 4). Thus, the PFAD was spiked with OCDF (test B5) to monitor the dechlorination of the congeners during the hydrogenation, and the results were compared with those of OCDD (test B2).

The rate of dechlorination of OCDF (Fig. 4c and d) was higher than that of OCDD (Fig. 4a and b), as reflected in the decrease of the blue bars. In the OCDF test, the IV (5 g I₂/100 g) showed full hydrogenation after 240 min, and the concentration of OCDF decreased to 201 ng/kg; after 270 min under similar hydrogenation conditions, the concentration of OCDD was 1446 ng/kg (Fig. 4a). At this stage, the concentration of the regulated lower-chlorinated PCDF congeners (red, orange, and yellow bars) was lower than the non-regulated ones (dark and light green bars) (Fig. 4c). However, as shown by Fig. 4d the TEQ level (17 ng WHO₂₀₀₅-PCDD/F-TEQ/kg) is significant higher than the regulatory limit at 240 min and further increased afterwards at 330 min while the congener concentration further decreased. The contribution of the regulated lower-chlorinated PCDF congeners with higher TEFs resulted in this exceeding of the maximum level, the highest contribution coming from

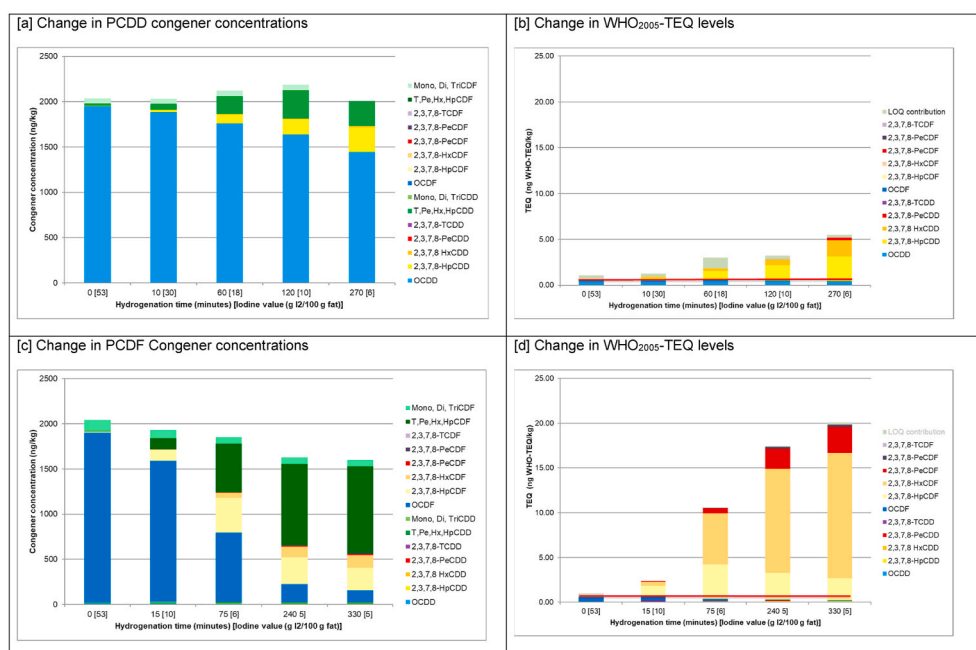


Fig. 4. Effect of the hydrogenation of palm fatty acid distillate (PFAD) on the dechlorination of octachlorodibenzo-p-dioxin (OCDD) (a) and -furan (OCDF) (c), and the impact on the TEQ level (b and d); hydrogenation conditions 170 °C, 0.3% catalyst, and 30 bar. On the X-axis, the Iodine Value is shown between brackets as indication of the hydrogenation grade.

the regulated HxCDFs. Also, in the OCDD test, the TEQ level (5.5 ng WHO₂₀₀₅-PCDD/F-TEQ/kg) exceeded the legal limit at the end of the hydrogenation (IV 5 g I₂/100 g), but it was lower than that for OCDF. In both cases, the regulated congeners TCDD and TCDF with high TEF values, 1 and 0.1, respectively, were not detected, contrary to the regulated penta, hexa and hepta congeners (Fig. 4).

According to Murena and Schioppa (2000), two parameters could contribute to the determination of the dechlorination rate of polychlorinated biphenyls (PCBs): (i) the nature of atoms adjacent to the chlorine atom that is substituted, and (ii) the position of the chlorine atom with respect to the phenyl bond. The dechlorination rate is higher when the chlorine atom is positioned between two hydrogen atoms, whereas it is lower when both adjacent atoms are chlorine atoms, and if the chlorine atom is in the ortho-position (Murena & Schioppa, 2000; W. Wu, Xu, Zhao, Zhang, & Liao, 2005). Zhang et al. (2007) investigated the dechlorination selectivity on the different substituted positions for OCDD. They noticed that the 2-position had a higher reactivity than the 1-position, but the difference was small. They also observed that OCDD converted into the non-regulated 1,2,3,4-TCDD when the dechlorination was incomplete. However, no regulated 2,3,7,8-TCDD was detected after the hydrogenation of OCDD. Likewise, we found that the regulated 2,3,7,8-TCDD and 2,3,7,8-TCDF congeners were below the LOQ, while non-regulated TCDD/F congeners were detected (for example 1,2,3,4-TCDD and 1,2,3,9-TCDF) (Zhang et al., 2007). Gryglewicz and Piechocki (2011) described the main factors influencing the dechlorination rate of dioxin congeners. The first factor is the number of chlorine atoms; the higher the number of chlorine substituents on the ring, the more difficult the substitution proceeds (chlorine is considered an electron-withdrawing substituent). The second factor is the presence of electron-donating substituents, such as NH₂ and CH₃. The third factor is steric hindrance, and the fourth factor is the affinity of reagents to the catalyst surface (Gryglewicz & Piechocki, 2011). The lower dechlorination rate of OCDD compared to that of OCDF (Fig. 4a and b versus 4c and d) might have been due to steric hindrance.

3.4. Pilot-scale samples compared with commercial monitoring samples

A spiking test was performed to investigate if the findings of the pilot study with OCDD concentrations measured in commercial products were comparable with those of the samples from the commercial hydrogenated palm fatty acid distillate (Fig. 1, sample point B) (Taverne-Veldhuizen et al., 2020).

Fig. 5 depicts the result of the hydrogenation of PFAD loaded with 99.8 ng/kg OCDD (test B6) compared with the five monitoring results of commercial HPFAD. The concentration of OCDD was based on the average OCDD concentration in PFAD monitoring samples plus one-time the standard deviation. As only OCDD was detected in commercial PFAD samples, this test was only performed with spiked OCDD. Fig. 5 shows that the TEQ value of the fully hydrogenated spiked sample after 90 min and 240 min of hydrogenation (1.21 ng and 1.31 ng WHO₂₀₀₅-TEQ/kg) exceeded the regulatory level. As found in the other tests, when hydrogenation continued, the congeners became lower chlorinated. The TEQ value of the spiked sample fits in the range observed for the commercial HPFAD monitoring samples.

The present study confirmed that the hydrogenation of PFAD might result in an increase in WHO₂₀₀₅-PCDD/F-TEQ, whereby the TEQ level could exceed the legal limit. Four notifications related to HPFADs were reported in the EU RASFF database (period 1999–2014), and those levels (maximum 1.47 ng WHO₂₀₀₅-TEQ/kg for RASFF (Directorate-General for Health&Consumers, 2011)) corroborate the results reported in Fig. 5. However, there were no alerts related to hydrogenated palm oil. Thus, the likelihood of exceeding the regulatory limit depends on the presence of dioxin congeners, the hydrogenation degree of the product, and the type of matrix that is hydrogenated (e.g., refined palm oil or PFAD). Present study shows that the chance of exceeding the maximum level can be managed by hydrogenation of OCDD to non-regulated congeners or reduction of the OCDD concentration in the product to be hydrogenated.

4. Conclusions

The present study showed that the dechlorination of highly

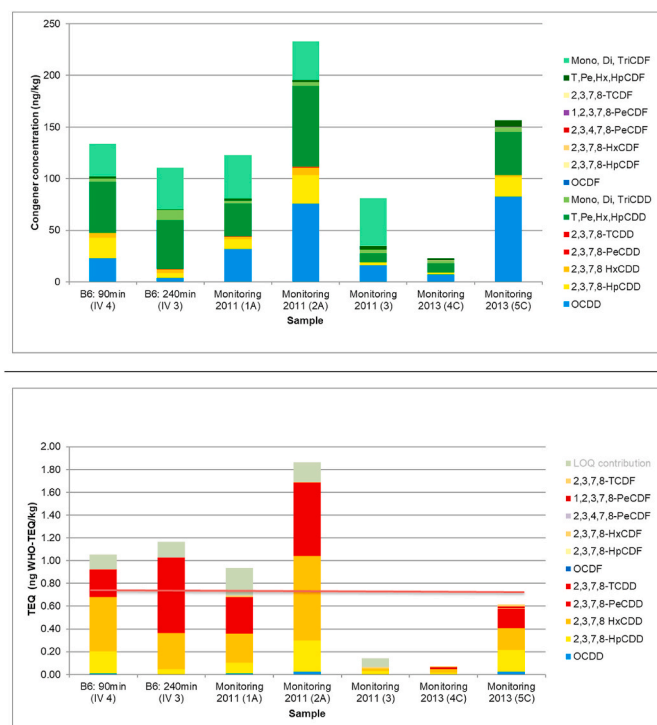


Fig. 5. Congener concentration and its toxic equivalents (WHO₂₀₀₅-TEQ) in fully hydrogenated palm fatty acid distillate (HPFAD) samples; PFAD spiked with 99.8 ng/kg octachlorodibenzo-p-dioxin (OCDD) after 90 and 240 min hydrogenation (test B6) as compared to 5 HPFAD monitoring samples (2011–2013).

chlorinated dioxin congeners during the hydrogenation of refined palm oil and PFAD decreased the total concentration of dioxin congeners. The lower-chlorinated congeners with a higher TEF were formed in the first phase of the hydrogenation increasing the TEQ level. However, when the hydrogenation continued, the dechlorination continued as well. Consequently, the concentration of regulated congeners further decreased, leading to a decrease in the TEQ level. Moreover, the current study indicated that the position of the chlorine atoms on the dioxin congeners present in PFAD affects the dechlorination effectiveness (type of formed congeners) and efficiency (dechlorination rate). The regulated congeners TCDD and TCDF with high TEF values, 1 and 0.1, respectively, were not detected, contrary to the regulated penta, hexa and hepta congeners. Additionally, a higher catalyst dose, hydrogenation temperature, and pressure increased the dechlorination rate. Furthermore, PCDFs dechlorinated faster than PCDDs.

As OCDD is the main congener in the crude palm oil and palm fatty acids made thereof, our findings possibly explain the RASFF alerts for HPFADs, whereas so far, there have been no alerts for hydrogenated palm oil.

Declaration of competing interest

No conflict of interest authors.

CRediT author contribution statement

Wilma Taverne-Veldhuizen: Conceptualization, Methodology, Investigation, Visualization, Writing – original draft, Preparation. **Ron Hoogenboom:** Conceptualization, Writing – review & editing. **Guillaume ten Dam:** Methodology, Formal analysis. **Rik Herbes:** Conceptualization, Methodology, Writing – review & editing. **Pieterneel Luning:** Conceptualization, Validation, Visualization, Writing – original draft, Preparation.

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