IEA Bioenergy
Technology Collaboration Programme

Assessment of individual compounds for DTL oil safety aspects

Considerations for R&D work

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INTRODUCTION

During research and development of DTL process, many people (technicians, laboratory etc) are exposed to DTL oils, often with (partially) unknown chemical composition. It is always important to be aware of the possible hazards; a fact that is reflected by national regulations to protect workers, consumers and the environment. Detailed chemical composition is required in most cases to meet national regulations for safe handling of chemicals and all people involved in handling DTL oils. Unless DTL oils are introduced as marketable commodity, which implies a readily available set of hazards associated with this substance in most countries, it is important to be aware what kind of chemical compounds are relevant for hazards to be able to quickly react and assess protective measures.

The only official registration available at the moment is the European REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) dossier of fast pyrolysis bio-oil (FPBO) based on woody feedstocks (CAS 1207435-39-9)[1]. It is registered as chemical substance with unknown or variable composition, complex reaction products or biological materials (UVCB). Further specifications are given and it is likely that DTL oils from other feedstocks and/ or processes show significant deviations so that they cannot be traded within this REACH dossier.

In the following we will provide some examples of possible hazards in conjunction with DTL oils and how they are influenced by chemical composition. This presentation is limited to a reduced set of substances available from literature, which by no means replaces a full safety assessment required to meet national regulations for the specific DTL oil in question. The aim is to guide towards critical compounds reported in literature and also to keep track of single chemical compounds during R&D activities.

The examples are based on evaluation of chemical mixtures according to the CLP regulation (classification, labelling and packaging)[2] that aligns the system for classification, labelling and packaging of chemical substances and mixtures to the Globally Harmonized System (GHS). As such, it complements the 2006 REACH Regulation of the EU[3]. We have chosen two publications that feature detailed analyses of produced FPBO fractions for varying feedstocks (see Table 1).

IDENTIFICATION OF CRITICAL COMPONENTS FOR HAZARDOUS POTENTIAL OF DTL OILS

Toxicity (oral/ dermal/ inhalation)

Toxicity of a mixture is estimated according to CLP regulation by summing up the individual toxic potential weighted by concentration of each compound present in a quantity ≥1%[4]. Hardly any substance in DTL oils is relevant for this estimation of mixture toxicity. There is a

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[1] https://echa.europa.eu/registration-dossier/-/registered-dossier/12235, last accessed March 2022

[2] Full title: Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.

[3] https://en.wikipedia.org/wiki/CLP_Regulation, retrieved September 22nd, 2021

[4] This is a simplified explanation. Technically, the reverse of the lethal dose of each substance is multiplied by its concentration and added up; the reverse of the resulting sum is then used as indication for the toxicity of the mixture, i.e. the higher the lethal dose the lower the toxic potential.

number of substances in the range between 0.1 and 0.5% that are categorized Acute Tox. Cat. 3 or 4 (e.g. phenol, furaldehyde, cresols). It is not much of a surprise that even if considering these substances according to the method applied in CLP regulation, one ends up with a toxicity estimate of typical DTL oils far from even the lowest category. It follows that for this example, no Acute Toxicity category is resulting, neither for oral, dermal or inhalation exposure.

Skin Corrosion/ Eye Damage

Evaluation of skin corrosion potential is comparably straightforward for most DTL oils due to the pervasive presence of acetic acid. Highest category Skin Corr 1 is applicable for an additive concentration of at least 5% of substances that fall in the hazard class Skin Corr 1. This is reached for FPBO in many cases. The hazard potential of a mixture is lowered to Skin Irrit 2 for an additive concentration of ≥1% but <5%. FPBO has a variety compounds relevant for such a classification and care should be taken to at least take measures against Skin Irrit 2 hazards.

The presence of acetic acid and other acids with category Skin Corr. 1 also directly influence evaluation of eye irritation. It follows that for their concentration found in most DTL oils highest category Eye Dam. 1 is reached easily. For this an additive concentration of compounds classified as Skin Corr 1 of at least 3% is stated; this category is lowered to Eye Dam 2 between ≥1% and <3%.

Skin Sensitization

There are several substances present in DTL oils that fall under category Skin Sens. 1; typically between 0.1 and 0.5% (e.g. isoeugenol). CLP regulation does not implement additive rules to categorize mixtures and only individual concentrations ≥1% are relevant. It follows that DTL oils are rarely in the category Skin Sens 1[5].

Carcinogenicity/ Mutagenicity

Similar to sensitization, CLP regulation does not implement additive rules for compounds that fall under Carc Cat and Muta Cat. Instead, only individual concentrations ≥1% are relevant. Few of the compounds from Table 1 need to be considered here (e.g. furaldehyde, phenol) and they typically are reported in ranges between 0.1 and 0.5%. For the specific case of FPBO produced from sugarcane bagasse, 4-vinyl-phenol (CAS 2628-17-3) is reported in a concentration level >1%, which requires to classify a mixture with Muta 2.

Special compounds recommended for observation

Some compounds from Table 1 are observed in a range that could potentially affect the hazard potential of mixture if concentration increases slightly, be it due to a change in feedstock, reaction conditions, or enrichment by fractionation of the condensate.

From the substances listed in Table 1, Furaldehyde (CAS 98-01-1), Guaiacol (CAS 97-53-0), and Phenol (CAS 108-95-2) are recommended to be observed more closely for their impact on acute toxicity. This recommendation is based on their toxicity potential and, especially for phenol, since they sometimes are enriched as a target compound by research groups.

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[5] In the EU it is still required to label mixtures with EUH208 warnings if individual concentration of a compound with Skin Sens. 1 is ≥0.1%

In the presented examples, oil produced from sugarcane bagasse was reported to contain relevant amounts of 4-vinyl-phenol (CAS 2628-17-3). There is no data about lethal dosage available to estimate toxicity of a mixture containing that substance. Depending on the severity of its toxicity, 4-vinyl-phenol might lead to a classification of a compound mixture as Acute Tox even at the reported concentration level. This is a very good example that each specific produced DTL oil might contain single compounds that has a decisive influence on its hazard potential.

CONCLUSION

Following the methodology for mixture classification according to the European CLP directive, concentrations as summarized in Table 1 would lead to following classifications:

- Hard Wood: Skin Corr 1B, Eye Dam 1
- Softwood: Skin Irrit 2, Skin Sens 1, Eye Dam 2
- Wheat Straw Skin Irrit 2, Skin Sens 1, Eye Dam 2
- Sugarcane Bagasse Skin Corr 1C, Skin Sens 1, Eye Dam 1, Muta 2

While this evaluation reveals some insights as to which compounds influence hazard potential of the resulting mixture, it also becomes very clear that it is not able to describe the full hazard potential of DTL oils if the resulting classification is compared to the existing European FPBO REACH registration (which, e.g. also includes Carc. 1B and Asp. Tox 1).

The DTL oils presented in Table 1 focus on feedstocks with low amount of nitrogen and sulphur species. Especially nitrogen rich feedstocks are increasingly investigated for DTL, such as e.g. sewage sludge and microalgae. Chemical compounds in DTL oils produced from these feedstocks might change the overall picture in terms of hazards significantly.

Table 1: Summary of compunds reported for FPBO in selected scientific articles.

CAS		Hard-wood[a]	Soft-wood[a]	Wheat Straw[a,b]	SC Bagasse[c]	Skin Corr[d]	Skin Sens[d]	Toxicity[d]	Carc[d]	Muta[d]
64-19-7	Acetic acid	6.6	2.3	1.9	6.8	Skin Corr 1A				
141-46-8	Hydroxyacetaldehyde	1.6	3.7	0.6	6					
123-38-6	Propanal	0.9	0.8	0.5	0.6	Skin Irrit 2				
2134-29-4	Hydroxypropionaldehyde	0.7	0.5	-	0.6	Skin Irrit 2				
116-09-6	Hydroxyacetone	2.2	2.4	2.2	4.9			Acute Tox 4i,d		
	Sum of hydroxycyclopentenones and methylderivates	1.6	1.7	1.2	1.2	Skin Irrit 2	Skin Sens 1	Acute Tox 4		
497-23-4	Furanone,2-(5H)	0.6	0.6	0.2	0.6	Skin Irrit 2		Acute Tox 4o		
98-01-1	Furaldehyde	0.7	0.5	0.3	0.6	Skin Irrit 2		Acute Tox 3o,i/4d	Carc 2	
496-63-9	Pyran-4-one, 3-hydroxy-(4H)	0.5	0.4	0.3	0.2	Skin Irrit 2				
498-07-7	Levoglucosan	2.3	3.2	0.4	5.4					
108-95-2	Phenol	<0.1	<0.1	0.2	0.2	Skin Corr 1B		Acute Tox 3o,i/4d		Muta 2
	Cresols (sum of o, p and m isomers)	0.1	0.2	0.3	0.2	Skin Corr 1B		Acute Tox 3o,d		
90-05-1	Guaiacol	0.2	0.6	0.7	0.1	Skin Irrit 2		Acute Tox 4o		
93-51-6	Guaiacol,4-methyl-	0.1	0.8	0.6	0.1	Skin Irrit 2	Skin Sens 1	Acute Tox 4o		
97-54-1; 5932-68-3	Guaiacol,4-propenyl (sum of isomers)	0.3	1.2	1.3	0.5		Skin Sens 1			
91-10-1	Syringol	0.8	-	0.5	0.2	Skin Irrit 2	Skin Sens 1	Acute Tox 4o		
627-88-9	Syringol,4-(1-Propenyl)-	0.6	-	0.3	0.4	n/a	n/a	n/a	n/a	n/a
123-07-9	Phenol, 4-ethyl-	n.r.	n.r.	n.r.	0.6	Skin Corr 1C		Acute Tox 4		
2628-17-3	Phenol, 4-vinyl-	n.r.	n.r.	n.r.	1.5	Skin Corr 1B	Skin Sens 1	Acute Tox 1d/2i/3o		Muta 2
7786-61-0	Guaiacol, 4-vinyl-	n.r.	n.r.	n.r.	0.3	Skin Corr 1B				
121-33-5	Vanillin	n.r.	n.r.	n.r.	0.4	Skin Irrit 2	Skin Sens 1	Acute Tox 4o,i		Muta 2
498-02-2	Acetoguajacone	n.r.	n.r.	n.r.	0.3	Skin Irrit 2				

[a] Charon, N. et al Multi-Technique Characterization of Fast Pyrolysis Oils. *J Anal Appl Pyr* 116 (2015) 18-26
[b]organic rich condensate fraction
[c]Carriel Schmitt, C. et al From Agriculture Residue to Upgraded Product: The Thermochemical Conversion of Sugarcane Bagasse for Fuel and Chemical Products. *Fuel Process Technol* 197 (2020) 106199.
[d]https://echa.europa.eu/, last accessed March 2022

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