Advanced Sustainable BIOfuels for Aviation

Deliverable D1.1:

Technical Specification of Feedstock Quality

Consortium:

Acronym	Legal entity	Role
RE-CORD	CONSORZIO PER LA RICERCA E LA DIMOSTRAZIONE SULLE ENERGIE RINNOVABILI	CO
ENI	ENI S.p.A.	BEN
SKYNRG	SKYENERGY BV	BEN
CENER	FUNDACION CENER-CIEMAT	BEN
ETA	ETA – Energia, Trasporti, Agricoltura Srl	BEN
CCE	CAMELINA COMPANY ESPANA S.L.	BEN
JRC	JOINT RESEARCH CENTRE – EUROPEAN COMMISSION	BEN

CO…Coordinator, BEN…Beneficiary

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no. 789562

General Information

Call identifier: H2020-LCE-2017-RES-IA
GA Number: 789562
Topic: LCE-20-2016-2017
Start date of project: 01/05/2018
Duration: 4 years (30/04/2022)
Work Package: WP1
Type: Deliverable
Number: D1
Title: Technical Specification of Feedstock Quality
Due Date: 31/03/2022
Submission date: 31/03/2022
Reference Period: 06/2021 – 31/03/2022

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Responsible Person: Luca Sassi
Dissemination Level: Public

INTERNAL MONITORING & REVISION TABLE					
REV.	**DATE**	**DESCRIPTION**	**PAGES**	**CHECKED**	**APPROVED**
Final	31/03/2022		16	Yes	Yes

Document Type		
PRO	Technical/economic progress report (internal work package reports indicating work status)	
DEL	Technical reports identified as deliverables in the Description of Work	**X**
MoM	Minutes of Meeting	
MAN	Procedures and user manuals	
WOR	Working document, issued as preparatory documents to a Technical report	
INF	Information and Notes	

Dissemination Level		
PU	Public	**X**
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the Consortium (including the Commission Services)	
CO	Confidential, only for members of the Consortium (including the Commission Services)	
CON	Confidential, only for members of the Consortium	

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Context

European energy transportation sector

Nowadays the energy sector is facing an important challenge: supplying energy to a growing number of people and at the same time reducing GHG emissions (being CO_2 the main player).
The European Union, by the Green Deal, has revised its greenhouse gases (GHG) emission reduction targets to at least 55% by 2030 compared to 1990 levels, with the achievement of " net zero emissions" (scope 1, 2 and 3) by 2050.
The EU strategy, to achieve such ambitious goals, sets short and medium-term milestones that assume the development of renewable energy also by making the energy system more "circular" and efficient. In this view, biofuels and low carbon fuels are sustainable energy carriers produced from feedstocks that are intrinsically capable of regenerating and reproducing in a relatively short time, such as waste and residues from agricultural and forestry activities and related processing (both vegetable and animal substances) or as the biodegradable share of other wastes.

Renewable Energy Directive (RED) II – Directive (EU) 2018/2001 – set an overall binding renewable energy target of at least 32 % by 2030 with a 14 % target for the transport sector, with a clause for a possible upwards revision by 2023. Within this transport sector target, biofuels deriving from food and feed crops are capped at Member States (MS) 2020 levels up to 1 % higher, with a maximum cap of 7 % for each MS. If such a cap in a MS is less than 7 %, the country may reduce the transport target by the same amount. MS can also set a lower limit for conventional biofuels than prescribed in RED II. RED II also introduced two different sets of targets for feedstocks listed in Part A of Annex IX and feedstocks listed in Part B. The former must be supplied at a minimum of 0.2 % of transport energy in 2022, 1 % in 2025, and at least 3.5 % by 2030 and are double counted towards both this sub-target and the 14 % target. The latter, which nowadays only include UCO (Used Cooking Oil) and animal fats classified as categories 1 and 2 in accordance with Regulation (EC) No 1069/2009, will be capped at 1.7 % in 2030.
The revision proposal of the REDII Directive involves an increase in the European 2030 target from 32 % to 40 % of renewable sources in the energy mix, as the 32 % had been declared not sufficient according to the Climate Target Plan (CTP). As regards the transport sector, the Directive revision will bring in a radical change in the structure of the target: from a percentage share of equivalent energy, currently 14 %, to a reduction in carbon intensity of 13 % by 2030 will be pursued – if expressed with the current methodology, that would be equivalent to a reduction of 28 %. The double counting for biofuels from advanced feedstocks is likely to be eliminated and the percentage of advanced biofuels provided for in Annex IX A in the energy supplied to the transport sector will be presumably set at a minimum of 0.2% in 2022, 0.5% in 2025 and 2.2% in 2030. The cap on feedstocks listed in Annex IX part B is going to be raised.

Biofuel feedstocks

In January 2018, the European Parliament (EP) voted to ban the use of palm oil for the production of biofuels in the European Union (EU) by 2020, with the proclaimed aim to stop the deforestation of rainforests mainly in Indonesia and Malaysia.
A common way of categorization of biofuels is that made on the basis of the feedstocks used for their production. Biofuel can thus be divided into two main categories, namely “first generation

biofuels" and "second generation biofuels" – also known as "advanced biofuels" in coherence with RED II – which differ from the former as can be manufactured from various types of non-food biomass. These latter are indeed produced from advanced feedstocks that are listed in Annex IX Part A of the RED II, which includes some specific materials and some categories, all of them waste and residues.

To cope with the growing demand for biofuels and in order to meet the increasingly stringent sustainability criteria of international regulations[1], it is necessary to strengthen the supply chain of waste raw materials, not in competition with the food world, as main charges for the production of advanced biofuels.
Contrary to what happens for first generation biofuels, for which the feedstock supply chains are anchored to conspicuous and stable flows from the agricultural sector, the waste sector appears much more fragmented and requires great operational and logistical flexibility from biofuel producers

Currently, the availability of waste materials, such as used cooking oil and processing waste from the food and forage industry, is an issue that gives rise to perplexity. There are not many sound data on the topic – see, as for instance, the report "Used Cooking Oil (UCO) as biofuel feedstock in the EU" by van Grinsven et al., CE Delft, December 2020. Investments in the collection and pre-treatment chain are necessary in order to make these volumes available on the market.
The agricultural sector, with the development of oil crops with a low environmental impact in a broad sense, that is, for example, with a low ILUC (Indirect Land Use Change) impact, and not in competition with the food supply chain, can offer an additional basin supply of alternative charges.

Eni process for biofuel production

In this context, Eni has been investing a lot since late 90s in research projects as well as optimization of industrial deployment focused on the production of biofuels and bio-components for fuels.
Among these, the first process in temporal order born and realized is aimed at the conversion of vegetable oils to HVO (Hydrogenated Vegetable Oil), namely high-quality biofuel. The technology that allows this transformation is Ecofining™, patented in 2006 by Eni in collaboration with Honeywell UOP.
Scaling up the process on an industrial level enabled the conversion of two conventional refineries into bio-refineries, one in Venice – the first of its kind in the world – and one in Gela, which has helped revive the refining sector.

The Ecofining™ process involves the hydrotreating of vegetable oil in the 1st stage with the formation of a mixture of gases (mainly made of bio-propane) and linear paraffins (typically C15-C19 in case of palm-oil-like feedstock), which are isomerized in the 2nd stage, to give HVO diesel and HVO naphtha, that are the two bio-product of the whole reaction pathway together with the above mentioned bio-LPG (Ecofining™ process main reactions are shown in Fig. 1).
The process, therefore, clearly differs from FAME (Fatty Acid Methyl Esther) production, i.e. transesterification of vegetable oils with methanol, as it produces isomerized paraffins instead of oxygenates (which have poorer stability, less adequate cold properties, limited calorific value and lower miscibility with diesel of fossil origin).

[1] Implementing Act on the Sustainability of Biofuels, Bioliquids and Biomass Fuels having as its legal basis on Article 30(8) of RED II is being adopted by the European Commission with the objective of implementing provisions to ensure that compliance with the sustainability criteria and the reduction of greenhouse gas emissions, as well as the provisions on biofuels, bioliquids and biomass fuels with low or high risk of change direct and indirect land use, is verified in an efficient and harmonized way and in particular to prevent fraud

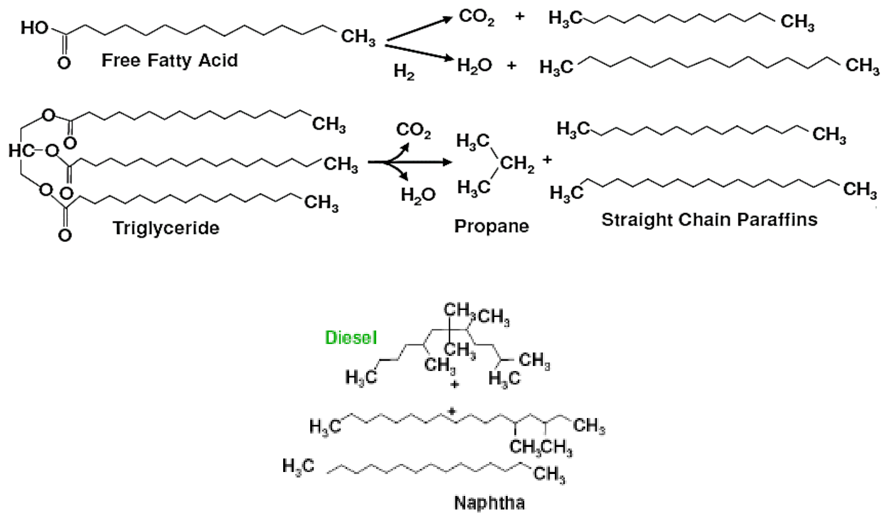

Figure 1. Ecofining^{TM} process main reactions for 1st stage (above) and 2nd stage (below) of the process, respectively

As depicted in Fig. 1, both free fatty acids (FFA) and triglycerides, or two ways in between consisting of monoglycerides or diglyceride, can represent the chemical composition of the feedstock.
FFA are hydrolysis products of triglycerides (TG) in vegetable oils. Very often they do not occur as such in biological systems: they instead occur as their esters, commonly triglycerides.
In edible oils, FFA formation occurs primarily during the production and the storage procedures of the oil and, in general, during handling of the raw material. Deterioration processes in lipids are additional sources of FFA. In the case of UCOs, the cooking process causes the vegetable oil triglycerides to breakdown to form mono-, diglycerides and free fatty acids.

For the sake of simplicity, in Fig. 1 only saturated carbon chains have been represented but feedstock for HVO can be composed by mono- or polyunsaturated fatty acids. An example of monounsaturated fatty acid is oleic acid, the most common monounsaturated fatty acid in nature (one of the 3 main fatty acids which palm oil is composed of): it is classified as a monounsaturated omega-9 fatty acid, abbreviated with a lipid number of 18:1 cis-9, very often referred to with "C18:1". The name actually derives from the Latin word "oleum", which means oil.

The number of unsaturations of a fatty acid carbon chain is of primary importance as it directly affects a different hydrogen requirement. Moreover, this latter is also affected by the intrinsic chemical difference existing between a fatty acid and a triglyceride, namely the glycerol group, that necessarily involves 3 more moles of hydrogen (1 mole for each carbon chain) for a triglyceride with respect to a fatty acid.
In any case, in the Ecofining^{TM} process any unsaturated carbons of the fatty acid chains are totally hydrogenated and the glycerol group, in the triglyceride molecules, is converted into propane.
As a rule, the right selection of feedstocks contributes to obtaining a high yield and proper quality in the desired product.

Some literature works exist on different vegetable oil sources for potential feedstock applications[2], but it is very hard to find a focus on a specific feedstock for a certain process.

[2] Int. J. Eng. Res. Technol. ISSN 0974-3154 Vol.13, No.3 (2020), pp. 500-519

UCO as a feedstock

UCOs can be generally sourced from households, HORECA[3] facilities and food processing industries.

UCO and EPFAD (Esterified Palm oil Fatty Acid Distillate) were the first types of feedstock supplied for the Venice biorefinery as alternatives to palm oil. Tallow instead have come more recently on Gela industrial plant due to permits and HSE aspects that require longer time; however, laboratory tests have started very early with respect to industrial processing.

Those feedstocks were at first co-fed with palm oil and processed in a pilot plant simulating the Venice biorefinery process.

Technology challenges were manifold. Feedstocks other than the most widely used palm oil imply different handling due for example to the poorer cold flow properties and organic acidity. This latter characteristic requires corrosion prevention for equipment along the whole system as also resulting acidic gases and liquids have an impact on the metallurgy of the circuit.

As a general, though unwanted, characteristic, typical of advanced biofeedstocks and UCOs/ animal fats is the high content of contaminants: mainly phosphorous, specific metals (such as iron), nitrogen, chlorides, and moisture.

Nevertheless, it has to be highlighted that vegetable oils and their non-toxic derivatives drastically reduce the content of sulphur and polycyclic aromatics in the final (bio)fuel with respect to the fossil fuel and, therefore, particulates emissions.

In order to handle and abate the above mentioned contaminants of biofeedstocks, in Venice, since May 2018, the POT (Palm Oil Treating) unit has been in operation, in order to reduce the content of contaminants in the feedstocks for the Ecofining™ catalytic process. This pretreatment step is made of two main units, degumming and bleaching, respectively designed to remove the Phospholipids/Gums from the crude vegetable oil and to minimizing its content of pigments (e.g., carotenes and chlorophylls), heavy metals, and the phosphorus remaining after degumming.

The higher the content of contaminants in the feedstock the higher the so called "start of run" temperature of the first stage of biorefining process (deoxygenation) is.

Deactivation of heterogeneous catalysts is an incumbent problem that causes loss of catalytic rate along with time.

It is possible to make projections on the life of the catalyst and on the catalytic process in general. While processing palm oil causes a certain level of catalyst deactivation, a higher deactivation is associated to a feedstock mix containing both palm oil and UCO / other feedstocks with higher contaminant level.

Moreover, the analysis of the liquid products out of the reactor (deoxygenated) gives indications on the level of the de-nitrogenation necessary to comply with the specifications of the following processing unit, which can definitely be affected by the type of feedstock and its contaminant.

With specific reference to UCO/RUCO supplied for the production of HVO diesel with improved cold properties (cloud point -18 °C) – to be distilled to obtain SAF – within BIO4A project, the geographical origin is predominantly Italian. It is hard to accurately establish the sector of origin (households, HORECA, other); however, the domestic share is statistically marginal compared to the overall quantities collected in Italy.

Nowadays RUCO is supplied to Venice biorefinery via truck by a pool of stable suppliers within a limited kilometric area.

[3] Hotellerie, Restaurants and Cafè.

Eni biofeedstock database

Similarly, as conventional refining cycles, biorefinery cycle needs to be optimized. Different typologies exist of alternative biofeedstocks potential substitutes of palm oil: their processability to the biorefinery processing cycle, related process yields, potential critical issues have been studied and evaluated by R&D internal unit.

A new «Eni Bio Crude Assay Database», together with proprietary analytical techniques and dedicated performance tests have been developed in the last 5-6 years and currently being used in order to characterize actual and potential feedstocks to Eni biorefineries.

Such data are stored in Eni reference Bio Crude Assay Database (Eni DB), aimed to describe and evaluate quality in feedstock purchase, critical issues and behavior in blending and storage, critical issues/opportunities related to behavior in processing cycle.

More than 380 biofeedstocks, each characterized with about 70 relevant parameters, and coming from more than 30 countries, are currently present in Eni DB so far, including by-products and wastes from industrial processes, UCOs, sustainable vegetable oils, animal fats and advanced biofeedstocks from Eni R&D projects.

Developed data are common knowledge within the company as are shared primarily with interested business units, such as Trading, Supply, Industrial Operations, Sustainability, Circular Economy.

Biofeedstocks data from Eni DB allow a quick and optimized supply choice and give useful information for industrial operations, since biofeedstocks availability is variable in time, both in quality and in volumes.

Relevant parameters for biofeedstock processing

Analysis of contaminants, mainly phosphorous, is relevant for determining possible pretreating (i.e., degumming and/or bleaching) steps and input to the Ecofining^{TM} process
Other contaminants critical at high concentration levels are moisture, nitrogen (poison for Ecofining^{TM} catalyst), chlorides (corrosion issues).
Oxidation stability determination gives an indication of fouling tendency typical of a feedstock.
Furthermore, Fatty Acids distribution and glycerides concentration are relevant for predicting hydrogen consumption and yield slate.

Quality variability in UCOs

Used cooking oils are waste vegetable oils. They have been used for cooking or frying in the food processing industry, restaurants, fast foods and at consumer level, in households.
The European Waste Catalogue (EWC) classifies them as Municipal Wastes (household waste and similar commercial, industrial and institutional wastes) including separately collected fractions, under the code 20 01 25 (edible oils and fats).

Figure 2. UCO batches collected in Eni laboratory storage

Several UCOs have been analyzed in Eni R&D laboratories, from several countries, showing a large variation in contaminants content, as reported in Tab.
UCOs contain impurities and water which have to be removed via several techniques before being used for further processing. After this treatment, UCO is converted into Regenerated Used Cooking Oil (RUCO) and supplied as a biofeedstock also for bio refining cycle.

Table 1 - Main chemical physical parameters analyzed in RUCOs: contaminants

Parameter	UOM	MIN value	AVG value	MAX value
Total Metals (Si, Fe, Al, K, Na, Mg, Ca, P)	ppm	0.8	138	3063
Chloride	ppm	1	21	198
Phosphorous	ppm	1.2	17	230
Total Nitrogen	ppm	7.5	152	2600

Regenerated Used Cooking Oil (RUCO) chemical-physical characterization

Several samples of RUCOs have been analyzed at Eni Downstream R&D laboratories during 2021, in order to monitor their quality as biofeedstoks to the Ecofining^{TM} process.

Figure 3. Typical RUCO samples appearance

Oxidation stability is low, as typical of RUCOs, due to thermal stress to which they have been undergone during cooking. Average values for such parameter are below 0.5 h.
In the following Tables the main chemical-physical parameters analyzed, and their ranges of variation are reported.
Quality of RUCOs depends both on the oil/fat used for cooking and on the food being cooked. Both elements affect primarily alkaline metals, chlorides (cooking salt) and nitrogen content (proteins) besides fatty acids distribution.
In Table 2 main contaminants content is reported. As it can be observed phosphorous concentration, if below a certain threshold, usually allows to skip degumming step and to pass directly to the bleaching step.
Nitrogen content typically does not reach high values; as a positive consequence Ecofining^{TM} catalysts activity is not affected.

Table 2 - Main chemical physical parameters analyzed in RUCOs: contaminants

Parameter	UOM	MIN value	AVG value	MAX value
Total Metals (Si, Fe, Al, K, Na, Mg, Ca, P)	**ppm**	**6**	**22**	**80**
Chloride	ppm	2,5	8,1	15,5
Phosphorous	ppm	3	9	30
Total Nitrogen	ppm	15	59	160

In Table 3 key fatty acids compositions data are reported, with respect to free fatty acids content, C chain length and saturated/unsaturated fatty acids, relevant for hydrogen consumption and yields.

Table 3 - Main chemical physical parameters analyzed in RUCOs: quality Fatty Acids content

Parameter	UOM	MIN value	AVG value	MAX value
FFA content	%m/m	3,6	9,0	17,9
Saturated	%m/m	11,6	15,5	25,3
Mono-unsaturated	“	44,2	50,1	58,9
Di-unsaturated	“	15,7	34,2	40,5
Tri-unsaturated	“	0,1	0,3	0,5
Avg C chain length	N. of C atoms	17,7	17,9	18,0

As it can be observed, fatty acids chain length is centered on C18, like the majority of oils, while there is variability on saturated/unsaturated fatty acids composition, with the widest variation ranges in Saturated and di-unsaturated fatty acids: in fact their minimum value is about 46 % of maximum in Saturated, and 39 % in di-unsaturated.

In Table 4 examples of fatty acids composition in two RUCO samples from different sources are reported.

Table 4 – RUCOs fatty acids composition by gas-cromatography

Sample nr.		Sample 1	Sample 2
Fatty acids composition	C length	% m/m	% m/m
Capric Acid	C10:0	0,05	0,05
Lauric	C12:0	0,05	0,05
Miristic	C14:0	0,10	0,90
Palmitic	C16:0	7,60	15,00
Palmitoleic	C16:1	0,20	1,90
Stearic	C18:0	3,40	7,80
Oleic	C18:1	46,60	56,40
Linoleic	C18:2	40,70	16,20
Linolenic	C18:3	0,20	0,10
Arachic	C20:0	0,50	0,60
Eicosenoic	C20:1	0,50	0,40
Beenic	C22:0	0,05	0,30
Erucic	C22:1	0,05	0,30

Table 5 reports a comparison of a sample of RUCO, RBD (Refined, Bleached, Deodorized) Palm Oil, Refined Palm Oil Mill Effluent (RPOME) oil and degummed soybean oil, all possible feedstocks to bio refining cycle – typically fed to Ecofining^{TM}. Key differences are highlighted in red.
POME, an advanced feedstock, is a waste generated from palm oil mills during palm oil processing. Its fatty acids composition is very similar to palm oil, but as a result of being derived from a partially degraded matter, it has a low oxidation stability and a higher FFA content.

Table 5 – Comparison among main various biofeedstocks chemical physical parameters

	UOM	REFINED PALM OIL	DEGUMMED SOYBEAN OIL	REFINED POME	RUCO	RUCO
FFA	%m/m	0,26	2,90	5,16	4,95	1,00
Total Metals (Si, Fe, Al, K, Na, Mg, Ca), P	ppm	6,0	17,7	21,0	80,0	6,0
Oxidation stability	h	**4,90**	**6,53**	**0,10**	**0,10**	**3,50**
N	ppm	8,10	5,60	11,00	160,00	35,00
Cl	ppm	5,80	60,00	15,20	14,40	4,80
P	ppm	<1	6,1	8,0	30,0	3
Saturated	%m/m	**49,7**	**15,5**	**49,8**	**25,3**	**12,4**
Mono-unsaturated	%m/m	**40,2**	**21,4**	**40,4**	**58,9**	**46,9**
Di-unsaturated	%m/m	**10,0**	**54,4**	**9,7**	**15,7**	**40,5**
Tri-unsaturated	%m/m	0,1	0,0	0,2	0,1	0,2
Fatty Acids Composition	%m/m					
C10:0		0,05	0,00	0,10	0,05	0,05
C12:0		0,20	0,00	0,20	0,05	0,05
C14:0		1,10	0,07	1,00	0,90	0,10
C16:0		**43,35**	**10,58**	**43,20**	**15,00**	**7,60**
C16:1		0,10	0,08	0,10	1,90	0,20
C17:0		0,00	0,09	0,00	0,00	0,00
C17:1		0,00	0,05	0,00	0,00	0,00
C18:0		4,50	4,00	5,00	7,80	3,40
C18:1		**40,00**	**20,93**	**40,10**	**58,50**	**46,80**
C18:2		**10,00**	**54,41**	**9,70**	**16,20**	**40,70**
C18:3		0,10	6,68	0,20	0,10	0,20
C20:0		0,40	0,31	0,20	0,60	0,50
C20:1		0,10	0,22	0,10	0,40	0,50
C20:2		0,00	0,04	0,00	0,00	0,00
C20:3		0,00	0,02	0,00	0,00	0,00
C22:0		0,05	0,30	0,05	0,30	0,05
C22:1		0,00	0,05	0,05	0,30	0,05
C23:0		0,05	0,04	0,00	0,00	0,00
C24:0		0,00	0,10	0,00	0,00	0,00
C24:1		0,00	0,04	0,00	0,00	0,00
Average C chain	%m/m	17,1	16,5	17,1	18,0	17,9

As it is observed, pristine vegetable oils, not being subjected to any previous stressing process, have higher oxidation stabilities and lower contaminants (e.g. Nitrogen, Metals).
It has to be highlighted the wide variability in fatty acids composition among the various feedstocks, with the highest di-unsaturated content in degummed soybean oil and the highest saturated content in RBD Palm Oil and its POME derived waste. As previously stated, RUCOs composition depends on oils/fats used for cooking and on cooked food: their qualities have a wide range.
Determination of chemical-physical parameters is a key step for optimization of processed blend and downstream operations and for upsets prevention.

Conclusions

All batches of RUCO supplied for BIO4A comply with quality specifications requested for feedstock processing to the degumming unit and are to Ecofining™ process. Their geographical origin is predominantly Italian. They are supplied to Venice biorefinery via truck by a pool of stable suppliers. Given that it is hard to accurately establish the sector of origin (households, HORECA, other), it can be stated that the domestic share is statistically marginal compared to HORECA and other industrial activities.