GOLD

Growing energy crops on contaminated land for biofuels and soil remediation

D2.1

Characterization of biomass materials and by-products, process considerations, balance of elements and recovery options - 1st version

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Partners

CRES - Centre for Renewable Energy Sources and Saving Foundation, Greece
AUA – Geoponiko Panepistimion Athinon, Greece
TUM - Technische Universität München, Germany
RE-CORD - Consorzio per la Ricerca e la Dimostrazione sulle Energie Rinnovabili, Italy
ETA - ETA Energia, Trasporti, Agricoltura, Italy
Uni-Lublin - Uniwersytet Marii Curie-Sklodowskiej, Poland
TNO - Nederlandse Organisatie Voor Toegepast Natuurwetenschappelijkonderzoek TNO, Netherlands
CERTH - ETHNIKO KENTRO EREVNAS KAI TECHNOLOGIKIS ANAPTYXIS, Greece
UNIBO - Alma Mater Studiorum - Università di Bologna, Italy
INRAE - Institut National de Recherche pour l'Agriculture, l'Alimentation et l'Environnement, France
YNCREA HDF – Junia, France
UNL - Universidade Nova de Lisboa, Portugal
ICL - Imperial College of Science Technology and Medicine, United Kingdom
WR - Stichting Wageningen Research, Netherlands
METE S.A. - METE AE METALLEFTIKI EMPORIKI TEHNIKI AE*MINING TRADING TECHNICAL SA, Greece
IITD - Indian Institute of Technology Delhi, India
HUNAN - Hunan Agricultural University, China
UDES - Université de Sherbrooke, Canada
IBFC - Institute of Bast Fiber Crops, Chinese Academy of Agricultural Sciences, China

Executive Summary

GOLD aims to bridge the gap between phytoremediation solutions on growing energy crops on contaminated lands and clean biofuel production, based on:

- Optimization of selected high-yielding lignocellulosic energy crops for phytoremediation, targeting different classes of soil pollutants.
- Establishing appropriate conversion techniques towards clean liquid biofuel production, utilizing biomass produced in contaminated lands.
- Integrated sustainability assessment of selected value chains for biofuels production and land decontamination.

In GOLD, two conversion routes have been identified for consolidating the appropriate conversion steps towards the production of clean low-ILUC (Indirect Land Use Change) biofuels from biomass grown in contaminated lands. These involve three pre-treatment options (slow pyrolysis, torrefaction, TorWash®), Entrained Flow Gasification (EFG), gas cleaning and syngas fermentation for the 1st route (European setting) and pre-treatment (grinding), high temperature autothermal pyrolysis, catalytic reforming and Fischer-Tropsch Synthesis (FTS) for the 2nd route (Canadian setting). Deliverable D2.1. includes, the characterization of contaminated feedstock (sorghum) from WP1, the evaluation of contamination level (inorganic contaminants) and the comparison of analyses performed by the partners of WP2.

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Introduction

The project

GOLD project aims to produce clean low Indirect Land Use Change (ILUC) biofuels by growing selected high-yielding lignocellulosic crops on contaminated land, and, in long-term, to return the polluted lands back to the agricultural production. This research project is organized in five work packages (Figure 1) and is mainly built on three pillars (WPs 1-3).

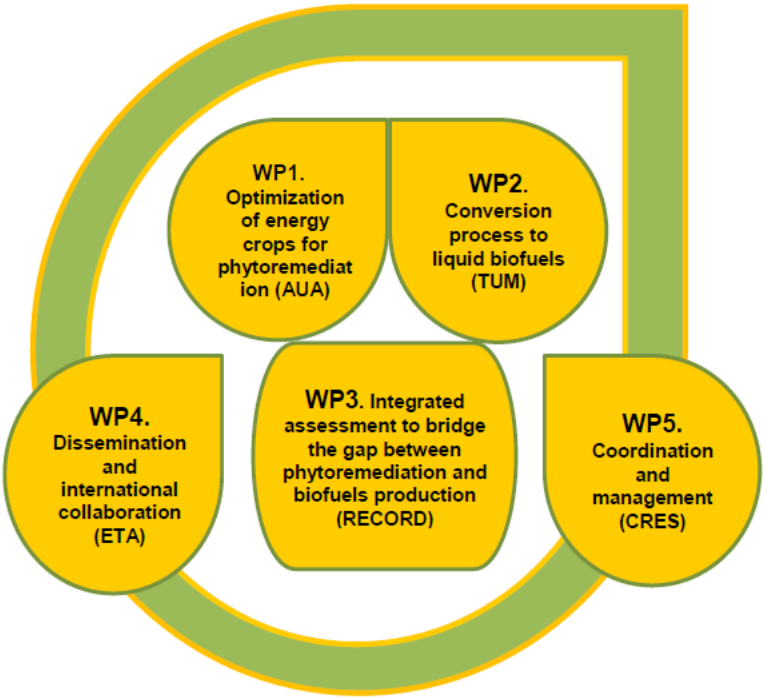

Figure 1: GOLD work packages

The first pillar (WP1) aims to optimize selected energy crops for phytoremediation as well as to develop optimized phytoremediation solutions for decontamination purposes. In the second pillar (WP2) the contaminated feedstock of WP1 will be converted to clean biofuels by developing two thermochemical based conversion routes; the first on gasification and the second on pyrolysis. In both routes the main contamination constituents will be collected in a concentrated form: mainly in a vitrified slag with low leachability produced in the gasification in the 1st and in a form of high-density biochar in the 2nd. In the third pillar (WP3) selected value-chains for biofuels production and land decontamination will be modelled and analysed in terms of cost, sustainability and Sustainability Development Goals (SDGs) for the creation of win-win situations. Emphasis is being given on the international collaboration towards Innovation Mission Challenge 4 on Biofuels with the participation of three highly consuming countries (Canada, China and India) throughout the value-chains.

Conversion process for clean liquid biofuel production (WP2)

Clean biofuels will be produced using the contaminated feedstock produced in pilot trials of WP1. Two conversion routes will be studied and evaluated: The *1st conversion route* (Figure 2) starts with biomass pre-treatment, where three options will be tested: Torwash (TNO), torrefaction (TNO) and slow pyrolysis (RE-

CORD). The pre-treated solids will be sent to TUM to feed the entrained flow gasifier (at temperatures of 1,300-1,500 °C), where the metal(loid)s will be collected in a concentrated form as slag or ash and the produced syngas after its cleaning will be used for a fermentation step to produce clean liquid biofuels (alcohols). The humic acids derived from the Torwash will be sent to WP1 partners to be tested as biostimulants in the 2nd half of the project. The *2nd conversion route* (Figure 2) will be based on an autothermal pyrolysis and FT synthesis to fuels, led by the Canadian partners (UdeS). Here, the pollutant recovery will take place via the pyrolysis char.

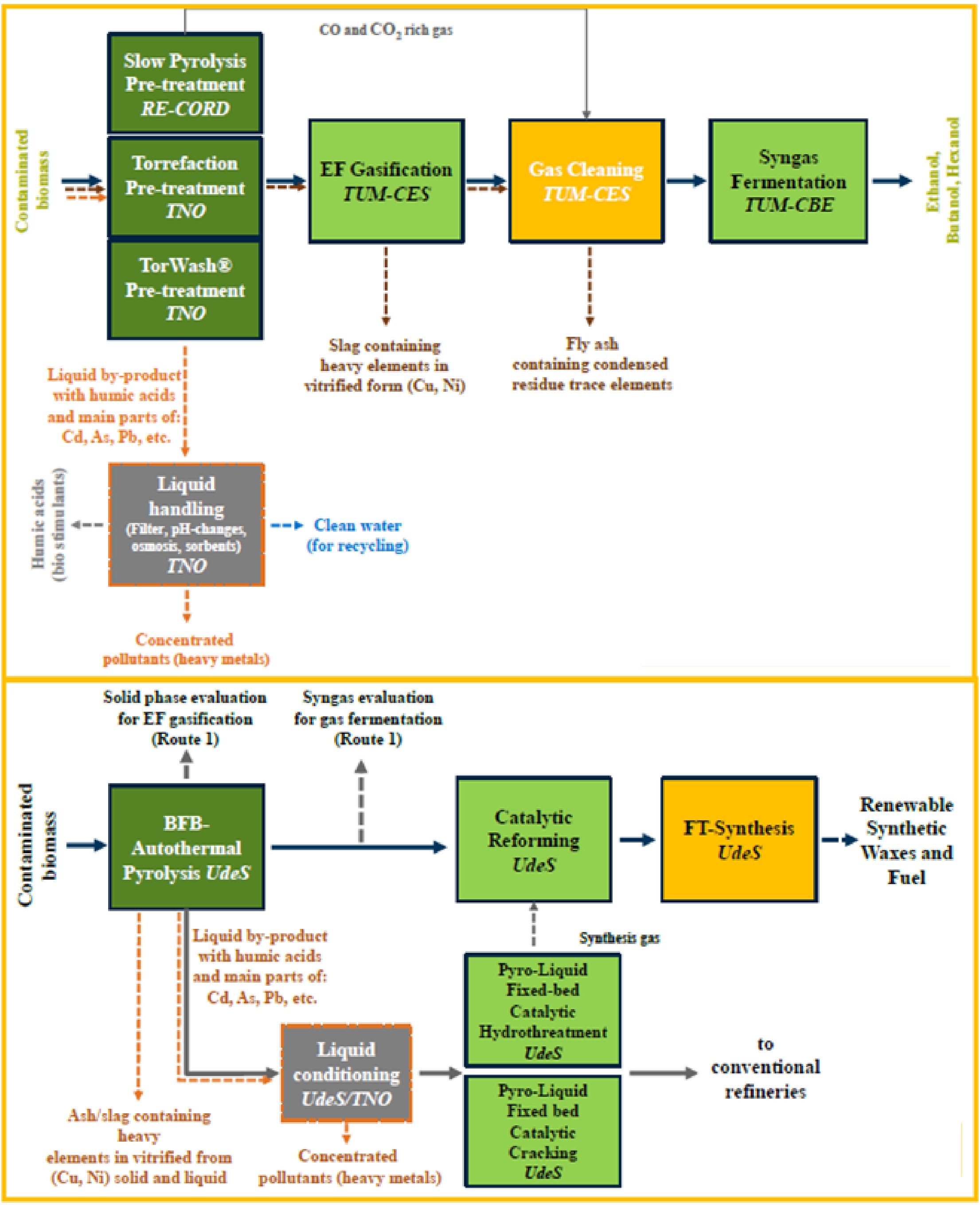

Figure 2: Contaminated biomass conversion routes

Table 1 presents WP2 specific objectives in relation to contaminated biomass conversion routes, with their success indicators to be met and respective target values.

Table 1: WP2 specific objectives with their respective indicators of success and target values

Objective	Indicators of success	Target value
• **1st route:** Carry out a high temperature gasification route with an optimized pretreatment producing non-leachable vitrified slag and subsequent fermentation into alcohol based liquid biofuels.	• Characterization of the produced biomass and by-products.	• Analysis of all crop samples (M48) and bio- products (M48) with focus on pollutants.
	• Torwash Process for biomass pre-treatment and separation / concertation of HM pollutants. • Humic acids collection from the liquid handling of the Torwash.	• Biomass from 4 crops will be Torwashed and 10 kg_{dry} solid material/crop will be provided for gasification (M24). • Humic acids to be tested as biostimulants in WP1; 10 L per crop (M24).
	• Torrefaction as pre-treatment to feed the gasifier (feedstock from organic polluted soils).	• 100 kg biomass from each of two crops will be torrefied and 50 kg_{dry} solid material will be provided for gasification (M24).
	• Slow pyrolysis as biomass pre-treatment for gasification.	• 10 kg_{dry} solid material for gasification per crop (feedstock from 2 crops) (M24)
	• Conversion of pre-treated biomass by entrained flow gasification into a high-quality and purified syngas.	• EFG characterization and lab tests (M36). • Syngas production and cleaning focusing on pollutants before fermentation (M48).
	• Syngas fermentation using a specialized bacterial strain to receive a liquid biofuel (C2-C6).	• Biofuel mixtures containing ethanol, 1-butanol, 2,3-butandiol and 1-hexanol will be produced (M48)
• **2nd route:** Carry out a pyrolysis-based route with the Subsequent upgrade of the pyrolysis products to refinery-compatible intermediates and FT-fuels (drop in fuels).	• Biomass characterization as well as all process derived products.	• All samples will be analyzed with focus on pollutants (M8 & M18).
	• Recovery, maximization and concentration of the inorganic pollutants in the BFB-ATP process.	• 5 kg/h BFB-ATP, 3 runs; 24 h each. • Products: solids with concentrated-metals, pyro-liquids, non-condensable gases (M24).
	• Conversion of the raw BFB-ATP liquid products into a conventional fossil fuel refinery compatible FCC feedstock.	• Catalytic cracking or hydrocracking, at least 5 runs; 200g of liquids per run. • Quality evaluation of the liquids and the resulting gaseous phase (M36).

	• Conversion of the raw BFB-ATP non-condensable products into a Fischer-Tropsch (FTS) compatible synthesis gas (SG).	• Catalytic reforming in steam, dry, mixed/tri and POX models for the conversion of the pyro-gas into a FTS-compatible SG. • At least 8 runs; 1l/min 24h each in an industrial reforming conditions reactor (M36).
	• Optimization of the FTS of SG into liquid biofuels. Special focus on optimization of the jet fuel fraction.	• FTS runs, at least 12 to 24-h duration runs of 200 ml/min gas feed in a fed-batch bubbled-slurry 3-ϕ reactor (M48).

The work for WP2 is organized in five tasks as presented in Table 2. Tasks 2.2 to 2.4 concern the 1st route and Task 2.5 the 2nd. Task 2.1 includes physical and chemical characterization of contaminated feedstock (WP1), products and by-products (WP2) using advanced analysis techniques to evaluate all technological options for both routes.

Table 2: WP2 work description

Conversion route	Task	Description
Both	2.1	Characterization of biomass materials and by-products, conversion process considerations, balance and recovery options of elements
1st	2.2	Biomass pre-treatment for entrained flow gasification (EFG)
	2.3	Entrained flow gasification and gas cleaning
	2.4	Syngas fermentation
2nd	2.5	High temperature autothermal pyrolysis and upgrading

Scope of the current document

Deliverable D2.1: Characterization of biomass materials and by-products, process considerations, balance of elements and recovery options – 1st version, is the first report of WP2. This deliverable provides an initial report on physical and chemical characterization of the contaminated biomass (sorghum) produced from WP1 (moisture content, elemental analysis, ash content, calorific value and concentrations of metal(loid)s). Characterization of the complete set of biomass samples of WP1 and conversion residues (bottom ash, leachates, fly ash by-products and samples from the syngas sampling), generalized element's mass balance closure for major trace pollutants, process and gas phase modelling as well as potential leachability and release pattern of trace pollutants, will be described in detail in D2.2: Characterization of biomass materials and by-products, process considerations, balance of elements and recovery options – Final version.

1 Conversion Process for Clean Liquid Biofuel Production

There are various technologies available for the valorization of lignocellulosic energy crops into advanced biofuels (several types of gasification and pyrolysis technologies, several types of pretreatments with fermentation) but not all of them can handle contaminants or render them in a concentrated form. Some technologies produce large volumes of effluents containing the contaminants in a dilute form (e.g., biomass fermentation, hydrothermal liquefaction and several intermediate temperature pyrolysis or gasification). High temperature gasification in entrained flow mode offers both the possibility of a clean syngas production as well as the vitrification of heavier metals slag. Pyrolysis based technologies offer the possibilities to retain most of the ash contents into the char. Therefore, within the framework of GOLD project, the clean biofuel production will be accomplished by two thermochemical conversion routes. In the first route, the contaminated feedstock will be pre-treated (by Torwash, torrefaction or low-temperature pyrolysis) and gasified at high temperatures securing the ash heavy metals in a condensed vitrified slag. The produced syngas, after cleaning, will subsequently be fermented to final liquid biofuels. The second route consists of a pyrolysis-based solution with the subsequent upgrade of the pyrolysis products to refinery-compatible intermediates and Fisher-Tropsch-fuels. In both routes the soil pollutants will be collected in a concentrated form. To ensure this outcome, it is essential to perform physical and chemical analyses of the contaminated feedstock and by-products from the conversion and pre-treatment processes. The analytical capabilities of the WP2 partners, as listed in Table 3, will be utilized for this purpose.

Table 3: Analytical capacity of WP2 partners

Partner	Description of the analysis
TUM, CERTH, UdeS	• Proximate analyses (fuels) and loss of ignition of solid samples
TUM, CERTH, UdeS	• Specific surface area-BET and pore size distribution studies
TUM, CERTH, UdeS	• Density, porosity, mineralogical and elemental analysis
TUM, CERTH	• Grain size analysis
CERTH, UdeS, RECORD	• Chemical analysis of major/trace elements by ICP-AES, ICP-MS, GHAAS, GFAAS, ICP-OES
CERTH	• Hg content using Au-amalgam-AAS for speciation of solid and gas samples
CERTH, UdeS	• Morphological and microchemical analysis by SEM-EDX, TEM
CERTH, RECORD, UdeS	• Thermogravimetric Analysis, TGA
TUM, CERTH	• Cl and F analysis by oxygen bomb combustion/ion selective electrode methods
TUM	• Direct analysis of flue gas composition
UdeS	• Direct analysis of pyrolysis liquid and gas composition by GC, HPLC
TNO	• Humic acid concentration and total organic carbon (TOC) in the Torwash effluent
TNO	• SEM work on the dried solid from TorWash to establish the heavy metal distribution

This document presents the first characterization results of contaminated sorghum, lab-scale slow pyrolysis char and TorWashed sorghum.

2 Characterization of Biomass Materials and By-products

In GOLD, the energy crops that will be used for conversion to biofuels (WP2) will be cultivated on and harvested from pilot fields on carefully selected real contaminated sites (WP1). As a first step, a number of pot trials were set up to evaluate different phytoremediation practices and to select the most promising in terms of: (a) soil remediation, (b) phytoextraction, (c) bioaugmentation, (d) plant growth, and (e) biomass productivity and quality. During the trial, the plants were monitored for phytotoxicity symptoms (chlorosis, necrosis, changed pigment contents, etc.) and for their growth (by measuring their height, number of leaves and tillers). During the harvest, the biomass produced per pot was weighed, and then divided into aerial biomass and roots. Analysis was conducted to determine the concentrations of metalloids and biomass quality characteristics. This information was then used to select the top two phytoremediation practices per crop for further evaluation in the pilot fields.

The pilot trials of the perennial crops were established in the 1st year of the project implementation, while the pilot small-scale fields for both annuals at the 2nd year and will be repeated in the 3rd. Starting from the second year, the top two phytoremediation practices were applied in all pilot fields. At the end of each growing period, the central part of each plot was harvested to estimate the biomass yield. Samples of the produced biomass were collected at the same time to monitor the moisture content and to conduct various laboratory analyses such as metalloid concentrations and biomass characterization. The concentrations of contaminants in sorghum plant tissues collected from the Agricultural University of Athens (AUA) field trials in Lavrion are presented in Table 4.

Table 4: Concentrations in sorghum plant tissues collected from the AUA field in Lavrion (mg/kg)

Sample	Contaminant (AUA analysis)					
	Pb	Zn	Ni	Cd	As	Sb
Control	47.23	354.43	0.85	11.98	0.34	0.04
Mycorrhiza	78.22	528.98	1.13	21.57	0.86	0.08
Mycorrhiza & Aminoacids	94.73	341.56	0.72	28.04	0.88	0.13

The whole plant material was homogenized, chipped, and then distributed among the WP2 partners (Table 5) to evaluate pre-treatment and conversion process parameters, as well as to conduct biomass characterization.

Table 5: Sorghum samples per WP2 partner

Partner	Quantity
CERTH	3 kg
TUM	1 kg
TNO	110 kg
RE-CORD	50 kg

The results of proximate, ultimate, and HHV/LHV analyses performed by partners of WP2 on sorghum samples received from the AUA field in Lavrion are displayed in
Table 6.

Table 6: Proximate, ultimate and HHV/LHV analysis of sorghum samples

Proximate analysis										
		a.r.			dry			daf		
		CERTH	TUM	TNO	CERTH	TUM	TNO	CERTH	TUM	TNO
H_2O	wt%	5.19	5.12	13.24	-	-	-	-	-	-
Volatiles	wt%	-	69.56	-	-	73.31	74.24	-	78.91	-
Ash	wt%	7.58	6.74	4.12	-	7.10	6.95	-	-	-
Fixed-C	wt%	-	18.59	-	-	19.59	-	-	21.09	-
Ultimate analysis										
C	wt%	-	38.17		-	40.23	43.93	42.31	43.30	-
H	wt%	-	5.77		-	6.08	6.01	5.87	6.54	-
N	wt%	-	1.15		-	1.21	0.90	1.08	1.31	-
S	wt%	-	0.19		-	0.20	-	0.13	0.22	-
O	wt%	-	41.43		-	43.66	43.15	50.74	47.00	-
Cl	wt%	-	1.45		-	1.52	-	-	1.64	-
HHV/LHV analysis										
		ar			dry			Daf		
HHV	kJ/kg	13,625.2	16,806.0	-	23,960.3	17,712.0	17,584.6	-	19,065.4	-
LHV	kJ/kg	12,208.1	15,413.9	-	12,877.0	16,244.9	-	-	17,486.1	-
Ash melting temperatures (TUM)										
550°C Imaging Carbon standard			Deformation			Hemisphere			Flow	
ox			898			1,202.7			1,235	

Furthermore, sorghum samples were analyzed for metal(oid)s concentration using Inductively Coupled Plasma (ICP) spectroscopy techniques. The results of the analyses from the various partners are presented in Figures 3-6.

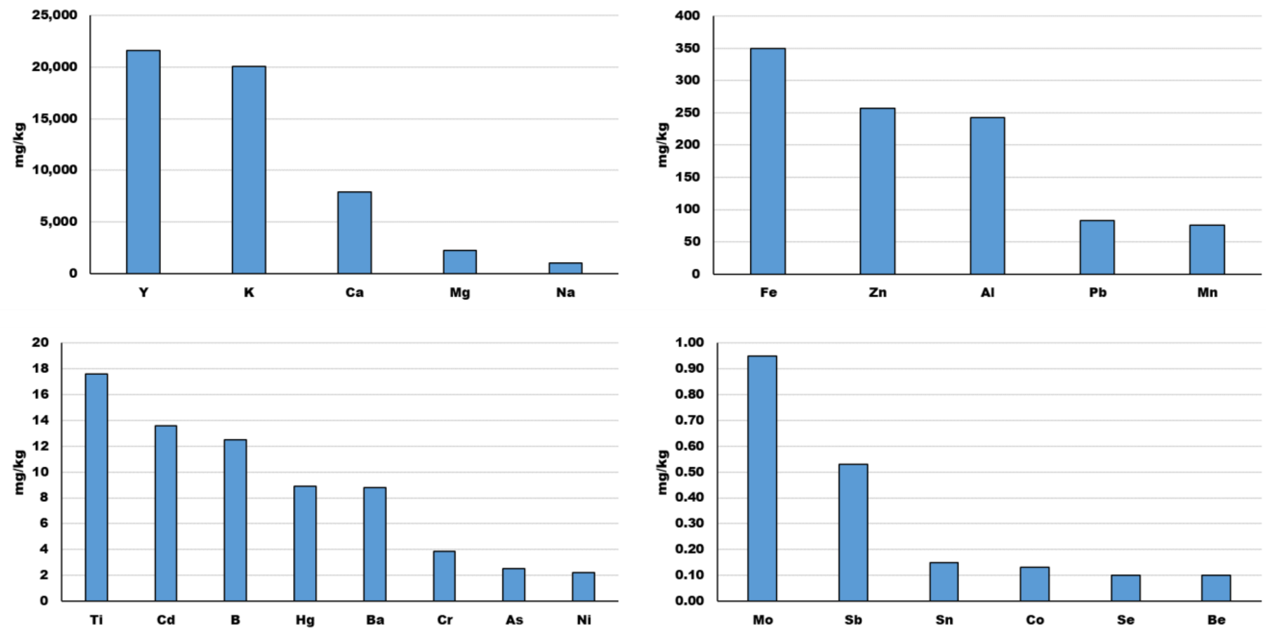

Figure 3: Elemental analysis of sorghum samples by CERTH

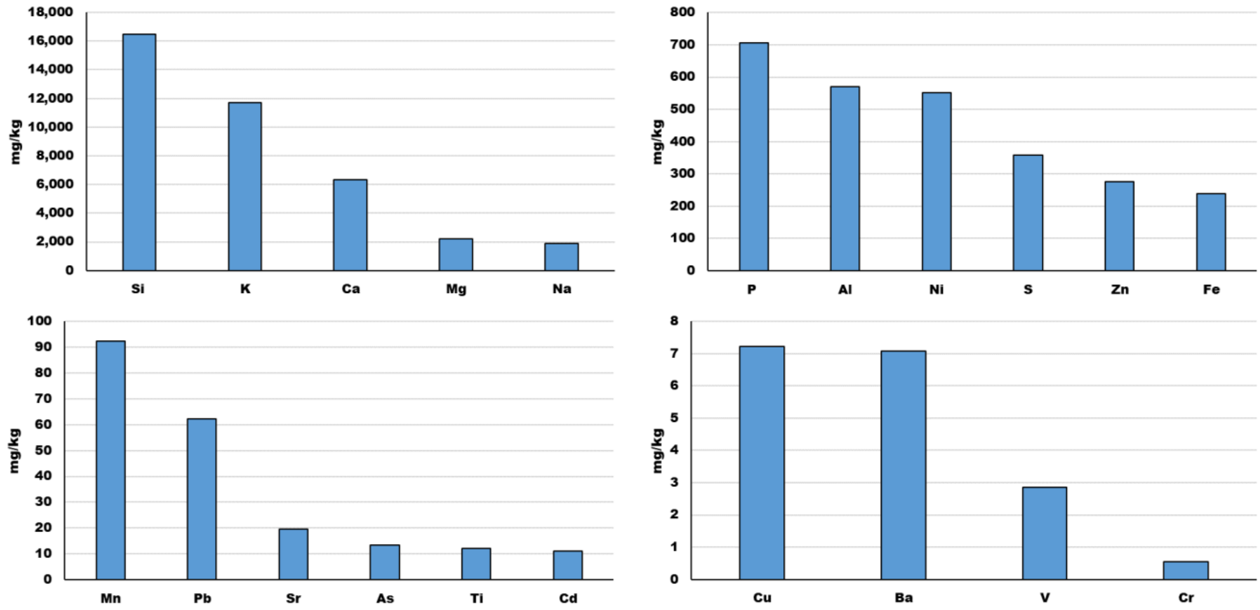

Figure 4: Elemental analysis of sorghum samples by TUM

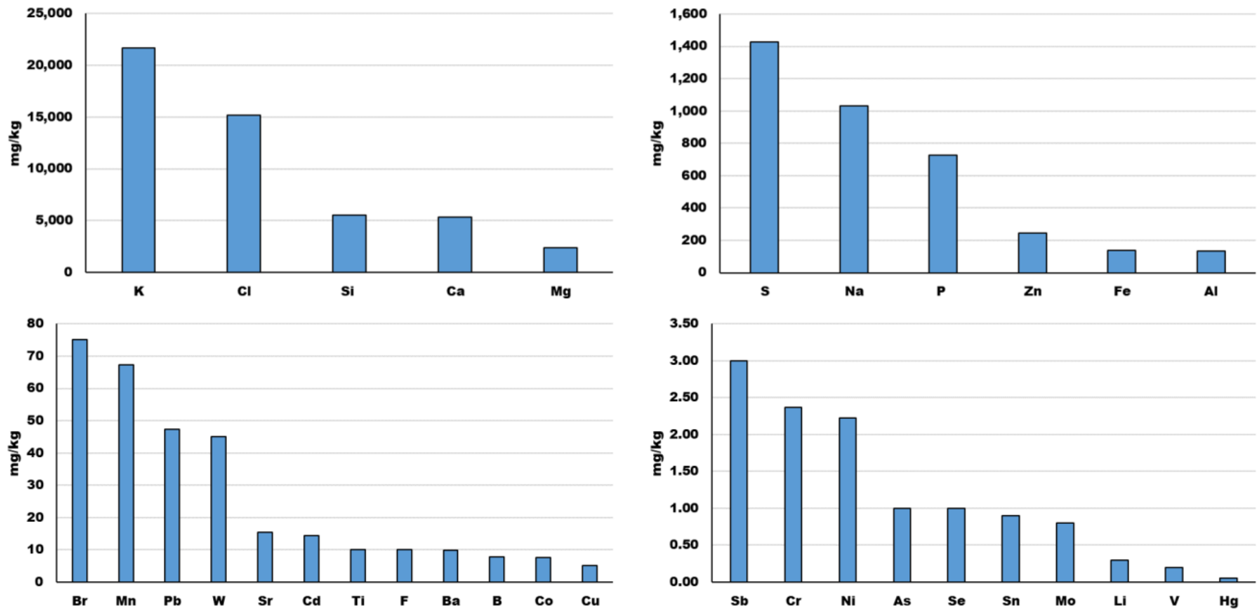

Figure 5: Elemental analysis of sorghum samples by TNO

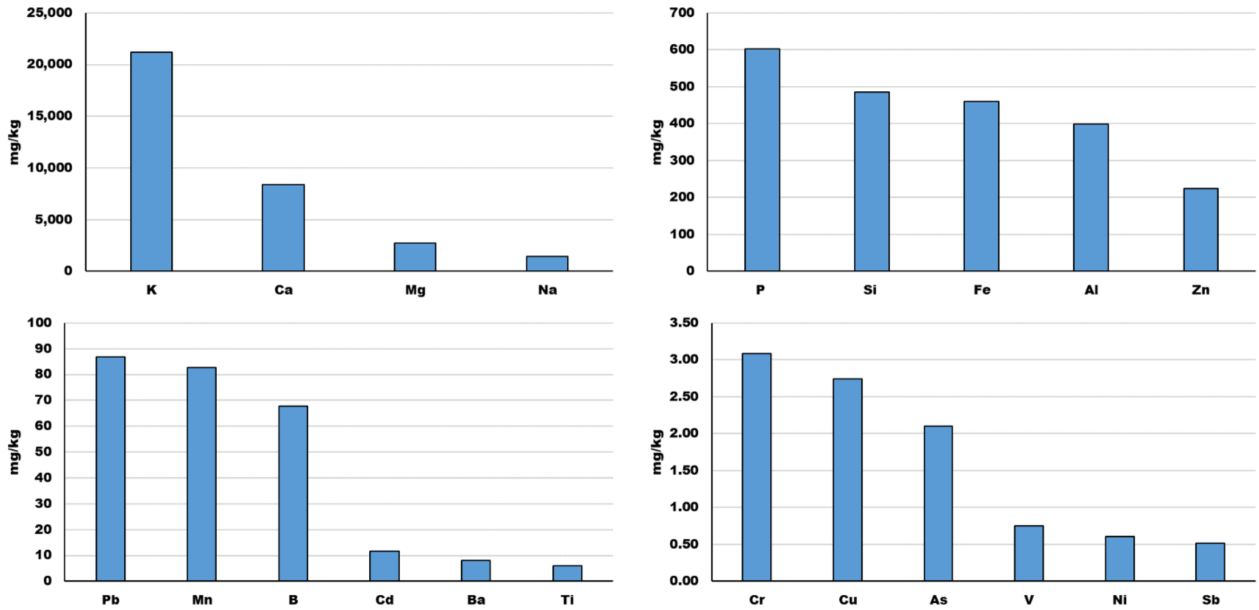

Figure 6: Elemental analysis of sorghum samples by RE-CORD (As and Sb by external lab)

TNO and RE-CORD conducted small-scale TorWash and slow pyrolysis tests to determine suitable process parameters as a preparatory step for Task 2.2, which focuses on pre-treating biomass for entrained flow gasification (EFG). Figure 7 presents the elemental analysis of six solid sorghum samples following TorWash treatment, while Figure 8 presents the elemental analysis of char for four different operational conditions.

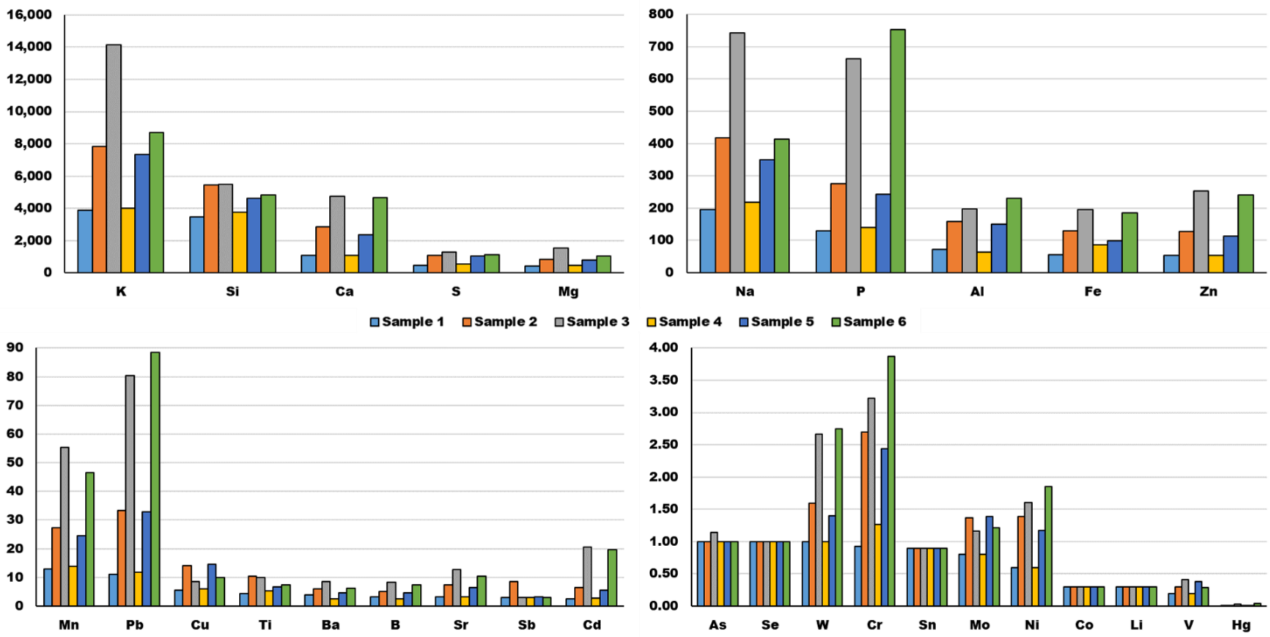

Figure 7: Elemental analysis of six TorWashed sorghum samples by TNO

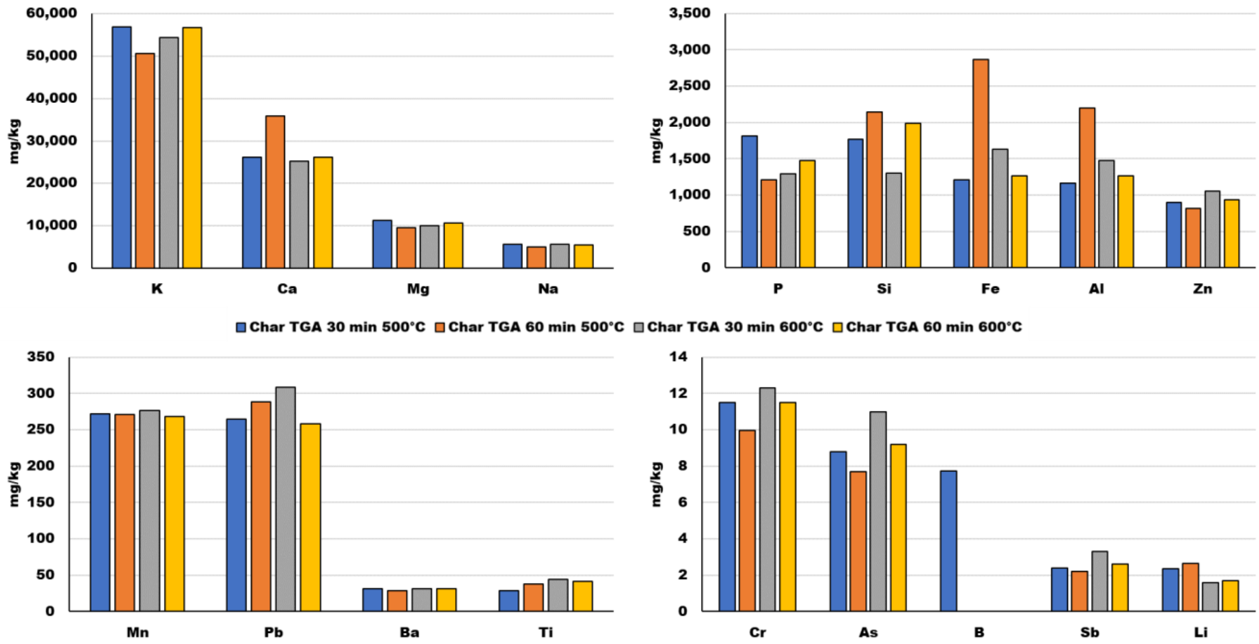

Figure 8: Elemental analysis of char for different operational conditions by RE-CORD (As and Sb by external lab)

Subsequently, RE-CORD evaluated the yield and the porosity (BET analysis) of char (Figure 9).

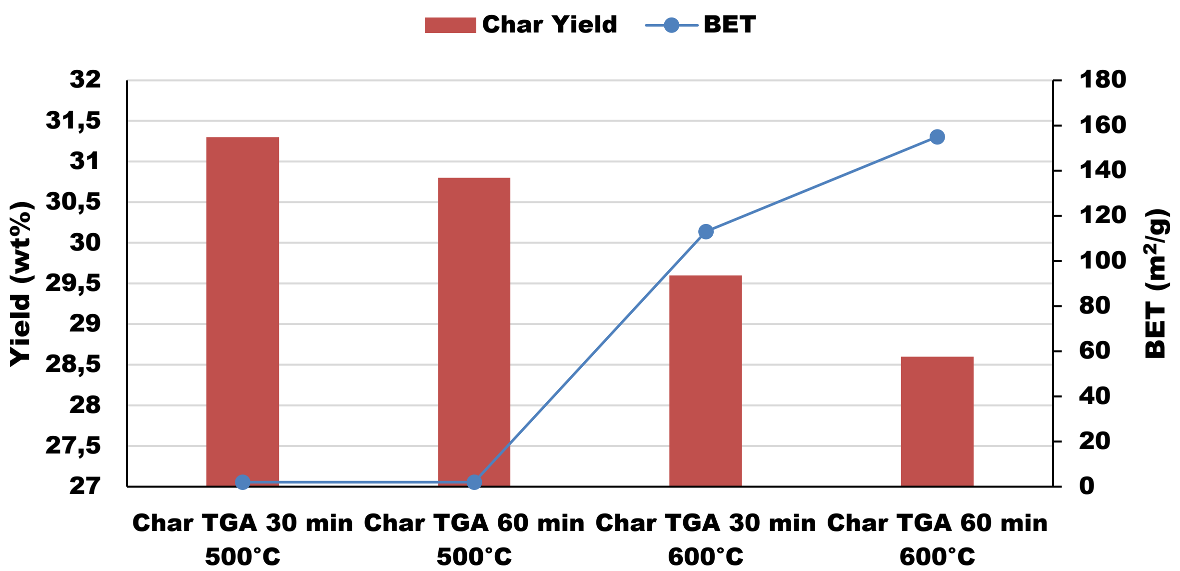

Figure 9: BET (surface area analysis) and char yield by RE-CORD

Based on the results, a temperature of 600 °C with a retention time of 30 minutes were selected as appropriate conditions for the slow pyrolysis tests.

Due to the synergies between WP2 partners, consistency, comparability and reproducibility of the analyses results are critical. Therefore, within the framework of Task 2.1, the analytical error from different analyses and sampling procedures will be identified, specified and jointly controlled with the aim to guaranty a common and comparative quality of the analyses. For this purpose, Table 7 presents the comparison of heavy metal and Zn concentration found in sorghum samples collected from the AUA field in Lavrion.

Table 7: Comparison of concentrations in sorghum samples collected from the AUA field in Lavrion (mg/kg)

Analysis	Sample	Contaminant					
		Pb	Zn	Ni	Cd	As	Sb
AUA	Sorghum – Control	47.23	354.43	0.85	11.98	0.34	0.04
	Sorghum – Mycorrhiza	78.22	528.98	1.13	21.57	0.86	0.08
	Sorghum – Mycorrhiza & Aminoacids	94.73	341.56	0.72	28.04	0.88	0.13
CERTH	Sorghum (whole plant)	83.4	257	2.2	13.6	2.5	0.53
TUM	Sorghum (whole plant)	62.2	276.6	551.9	11.1	13.3	-
TNO	Sorghum (whole plant)	47.4	245.4	2.23	14.4	<1	<3
RE-CORD	Sorghum (whole plant)	87	224	1	12	-	-
External lab (RE-CORD)	Sorghum (whole plant)	40	330	1.3	11	2.1	0.52

Slight variations in the results of the analyses presented by the WP2 partners may be attributed to several factors, including, differences in methodology or instrumentation, human error, and sample preparation. In this particular case, the latter is deemed as the most probable cause due to the heterogeneous nature of the sorghum samples. These differences are further highlighted by the results of elemental analyses of sorghum samples, presented in Figure 10.

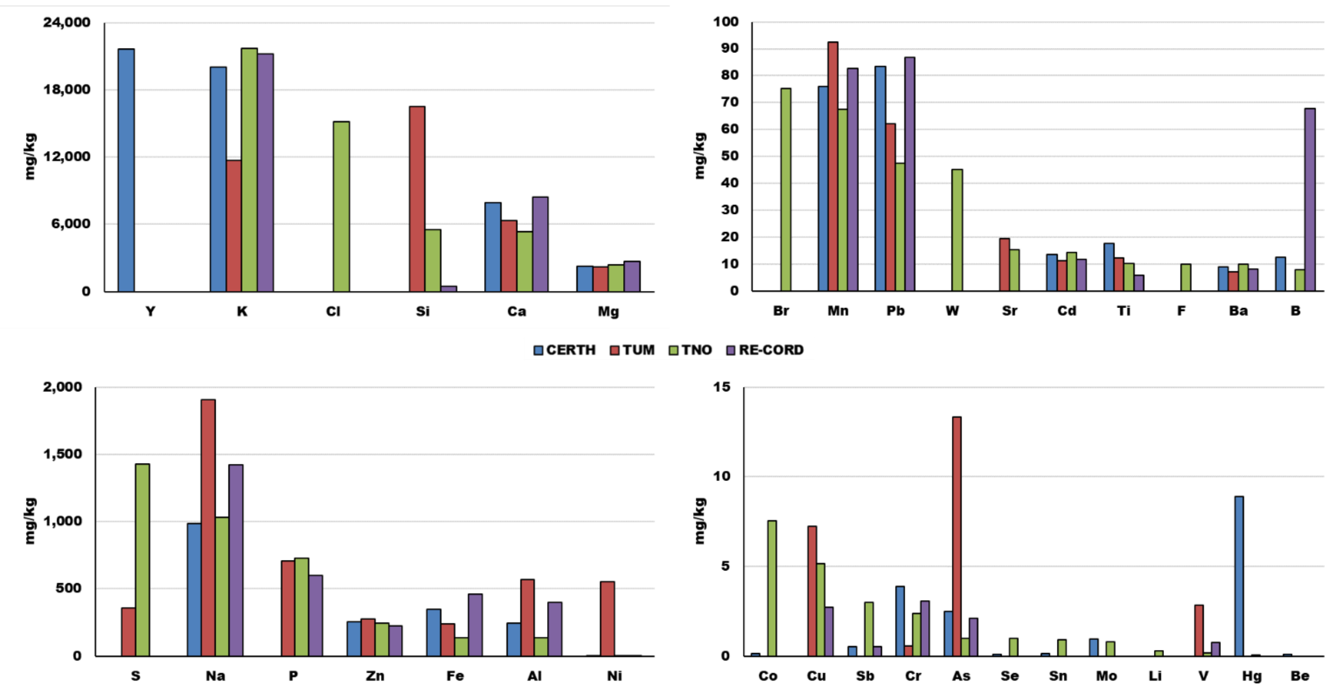

Figure 10: Comparative results of sorghum elemental analysis by WP2 partners

3 Exchange of materials within WP2 Partners

For the purposes of D2.2: Characterization of biomass materials and by-products, process considerations, balance of elements and recovery options – Final version, WP2 technology partners will deliver to CERTH biomass used and by-products (leachate, bottom and fly ash etc.) from the pre-treatment step and the EFG processes. CERTH will analyse all materials and compare results with any additional analyses performed.

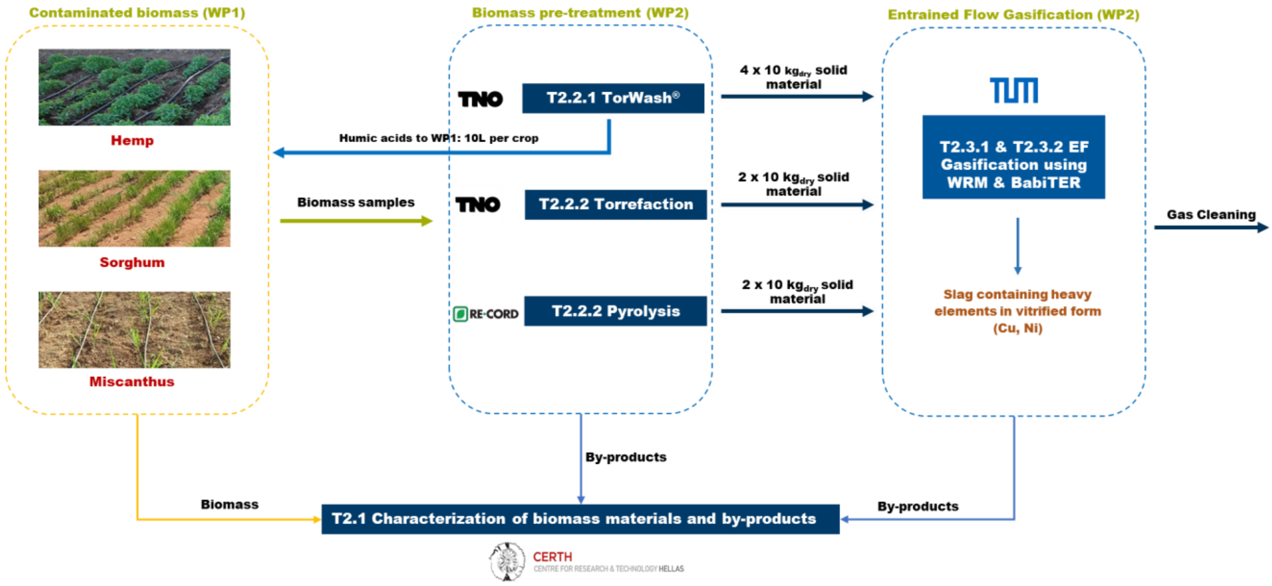

Figure 11: Material exchange between GOLD partners

WP1 partners will provide the remaining contaminated biomass samples and both CERTH and the partners mentioned in Table 3 will deliver the additional analytical results. The overall material exchange between GOLD partners is presented in Figure 11.