CONVERSION OF CONTAMINATED BIOMASS IN AN INNOVATIVE BIOREFINERY INTO HIGH-QUALITY ENERGY CARRIERS

Kick C.[1], Li T.[1], Daschner R.[1], Franke M.[1]

[1] Fraunhofer UMSICHT, Fraunhofer Institute for Environmental, Safety, and Energy Technology, An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany
Corresponding Author: Dr.-Ing. Christopher Kick; Tel: +49 9661 8155-436; E-mail: christopher.kick@umsicht.fraunhofer.de,
Address: Fraunhofer UMSICHT, An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany
B.Sc. Tingting Li; Tel.: +49 9661 8155-412; E-mail: tingting.li@umsicht.fraunhofer.de,
Dr.-Ing Robert Daschner; Tel.: +49 9661 8155-410; E-mail: robert.daschner@umsicht.fraunhofer.de,
Prof. Dr.-Ing. Matthias Franke; Tel.: +49 9661 8155-600; E-mail: matthias.franke@umsicht.fraunhofer.de.

ABSTRACT: Within the European-funded research project "Phy2Climate," an innovative biorefinery was implemented with the overall goal of combining phytoremediation and biofuel production. In the biorefinery, heavy metal-contaminated biomass harvested from the project's pilot sites was initially converted into gaseous, liquid, and solid intermediate products using the thermo-catalytic reforming process (TCR®). The aim of this study is to investigate the feasibility of converting heavy metal contaminated biomass (Rapeseed and Quinoa) into high-quality energy carriers using TCR® technology at post-reformer temperatures ranging from 550°C to 750°C. The results showed that increasing post-reformer temperatures significantly influenced product yields and quality. Lower temperatures favored the formation of bio-oil and bio-coke (commonly also referred to as biochar), while higher temperatures increased pyrolysis gas production, shifting the main energy carrier from bio-coke to gas. Heavy metal distribution varied: for Rapeseed, most heavy metals accumulated in bio-coke at 550°C, while for Quinoa, heavy metals were concentrated in bio-coke at 750°C. Higher temperatures resulted in higher H_2 yields and better HHV for both biomasses, with bio-oil with better HHV meeting ISO 8217 (2017) standards for low sulfur fuel oil. The study highlights a trade-off between maximizing favored product yields and concentrating heavy metals in bio-coke, suggesting further research to optimize TCR® processing conditions.
Keywords: biorefinery, thermochemical conversion, thermo-catalytic reforming, heavy metal, biofuel

1 INTRODUCTION

Within the scope of the EU-project "Phy2Climate" (GA-No. 101006912) an innovative biorefinery concept is developed to transform contaminated biomass from the pilot sites into high energy carriers. The biorefinery covers in a first step the conversion of the biomass into storable intermediates of higher energy density as the original feedstock. For this, the thermo-catalytic reforming process (TCR®) is used [1-4].

The conversion process is followed by subsequently upgrading the produced intermediates to standard biofuels according to Fig 1. The gas phase serves as a feedstock for a Gas-to-Liquid process (GtL) to produce oxygenated hydrocarbons with the aim of drop-in biofuel production in a conventional oil refinery. The oil phase is tested for marine fuel quality via distillation, the aqueous phase is purified while providing H_2 for the GtL process and the bio-coke could be a potential substitution for petrol-coke in the copper smelting industry. In addition, heavy metals accumulated within the bio-coke can be potentially recovered during the copper smelting process, closing the phytoremediation cycle [5].
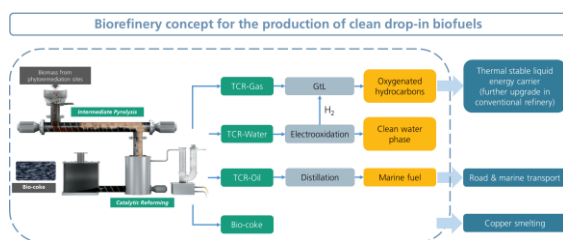
In this study, Rapeseed from Serbia and Quinoa from Argentina grown on heavy metal contaminated sites (dredged sediment disposal site in the case of Serbia, abandoned gold mine in the case of Argentina) were tested for the conversion. These plants are utilized in phytoremediation processes to effectively clean up soils that has been contaminated with heavy metals and metalloids [6-8]. Special attention of the conversion was given to the mass and energy distribution of the conversion products as well as to the heavy metal distribution.

2 METHODS AND EXPERIMENTS

2.1 Raw materials and pretreatment

Heavy metal contaminated Rapeseed from Serbia (Fig. 2.a) and Quinoa from Argentina (Fig. 2.b) are sourced from Phy2Climate partners' pilot sites. After harvest, the biomass is shredded, dried, and pelletized to make it reproducible for conversion. Heavy metals of concern in the biomass and the conversion products are Cr, Cu, Zn, Cd, Pb and Ni for Rapeseed and As, Cd, Cu and Zn for Quinoa.
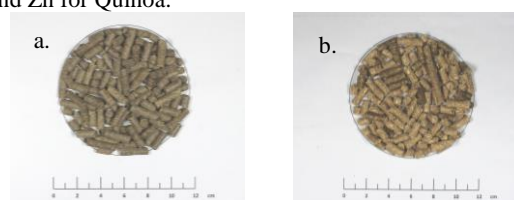

Figure 2: a. Rapeseed feedstock; b. Quinoa feedstock

Figure 1: Biorefinery concept

2.2 Thermo-Catalytic Reforming (TCR®) Process

A 2 kg/h lab-scale Thermo-catalytic reforming (TCR®) unit, combining intermediate pyrolysis with downstream post-reforming, is used for biomass conversion. The TCR®2 unit consists of a 15 L feeder, an auger pyrolysis reactor, a catalytic post-reformer, a condensate unit, an electrostatic precipitator (ESP), and a char container.

The Rapeseed and Quinoa feedstocks are processed at a reactor temperature of 450°C and post-reformer temperatures of 550°C, 650°C, and 750°C to compare product yields and qualities. After each experiment, the bio-coke remaining in the post-reformer and the char container is recovered and measured. The gas composition is measured instantaneously using a gas analyzer. The liquid phase products from both the condenser and the ESP are separated into oil and water via gravimetric and centrifugal techniques and then measured.

Following each experiment, the mass balance is determined by calculating the masses of the products and comparing them with the initial mass of the feedstock. Mass losses are attributed to the remaining bio-oil in the condensation unit due to the difficulty of collecting all the liquid produced and the process of separating the liquid phase into water and oil. The amount of gas produced is calculated by subtracting the total nitrogen used as purge gas from the total gas produced. In addition, the energy distribution of the conversion products is calculated. For this, the Higher Heating Values (HHV) of the products are multiplied by the mass fraction of each conversion product and standardized to 100%. This allows the individual energy content of the products to be related to the total energy content. Energy losses as heat during the process are not included in this calculation.

2.3 Heavy metal distribution

Heavy metal analysis was performed on biomass, bio-coke, bio-oil and water samples to investigate the behavior of heavy metals during the TCR process. Samples were wet digested with HNO_3 + HCl prior to elemental analysis. The concentrations of As, Cd, Cu, Cr, Ni, Pb, Zn in the digestates were determined using an Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) instrument.

The heavy metal distributions in bio-coke, bio-oil, and water after the TCR process were calculated from the elemental concentrations and end-product yields, while the results for gas samples were calculated by difference. The elemental recoveries in the four product fractions were determined using the following formulas:

$$\text{Element distribution in bio-coke (\%)}$$
$$= \frac{\text{total element concentration in bio-coke(mg/g)}}{\text{total element concentration in biomass(mg/g)}} \times \text{bio-coke yield(\%)}$$

$$\text{Element distribution in oil (\%)}$$
$$= \frac{\text{total element concentration in oil (mg/g)}}{\text{total element concentration in biomass (mg/g)}} \times \text{oil yield (\%)}$$

$$\text{Element distribution in water (\%)}$$
$$= \frac{\text{total element concentration in water (mg/g)}}{\text{total element concentration in biomass (mg/g)}} \times \text{water yield (\%)}$$

$$\text{Element distribution in gas/loss (\%)} = 100\%$$
$$\qquad\quad - \text{element distribution in bio-coke (\%)}$$
$$\qquad\quad - \text{element distribution in oil (\%)}$$
$$\qquad\quad - \text{element distribution in water (\%)}$$

3 RESULTS AND DISCUSSION

3.1 Mass and Energy balance

The mass balance and energy balance for Rapeseed and Quinoa products obtained at a reactor temperature of 450°C with increasing post-reformer temperatures of 550°C, 650°C and 750°C are shown in the Fig. 3 and 4.

The highest yields of bio-oil (8 wt%) and bio-coke were obtained at a post-reformer temperature of 550°C for both feedstocks, with rapeseed producing the most bio-coke at 36 wt%. As the reforming temperature increased, the gas yields also increased, with the highest yields observed at 750°C: 46 wt% for Rapeseed and 55 wt% for Quinoa.

In contrast, the yields of condensate (bio-oil and water) and bio-coke decreased with increasing post-reformer temperature due to secondary gas-bio-coke reactions at higher post-reformer temperatures. These data indicate that a higher post-reformer temperature favors gas formation at the expense of bio-coke and condensate yields.
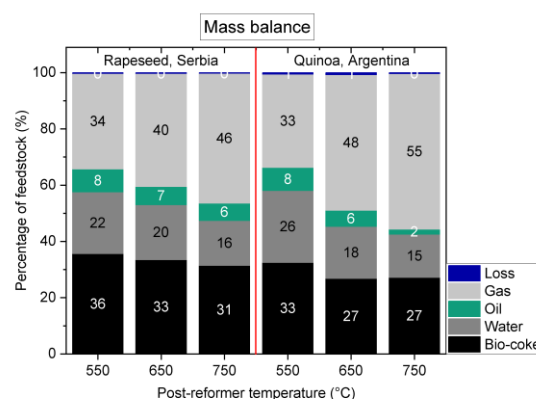

Figure 3: Mass balance of biomass conversion

The highest energy fraction for the lowest reforming temperature (550°C) was found for bio-coke with 56% for both Rapeseed and Quinoa. At 550°C, the energy yield of bio-oil and gas from Quinoa was higher compared to the Rapeseed trial, which can be explained due to the higher calorific value of the Quinoa bio-oil and gas, as shown in Table I.

Table I: Higher heating value of biomass and conversion products at different post-reformer temperatures (reactor temperature = 450°C)

Post-reformer temperature	°C	Rapeseed, Serbia			Quinoa, Argentina		
		550	650	750	550	650	750
Feedstock	MJ kg⁻¹	17.5	17.5	17.5	16.4	16.4	16.4
Bio-coke	MJ kg⁻¹	21.2	20.2	19.3	21.7	20.7	17.9
Bio-oil	MJ kg⁻¹	30.7	33.1	34.4	36.1	31.5	36.4
Gas	MJ kg⁻¹	9.9	12.0	14.0	7.5	11.5	13.0

At a reforming temperature of 750°C, the main energy carrier was the gas for both feedstocks. The

energy yields of the gas at 750°C were 44% for Rapeseed and 57% for Quinoa. Despite the lower HHV of the gas fraction for Quinoa at 650 and 750°C, the energy content of the gas phase was higher for Quinoa compared to Rapeseed due to higher amounts of syngas produced.
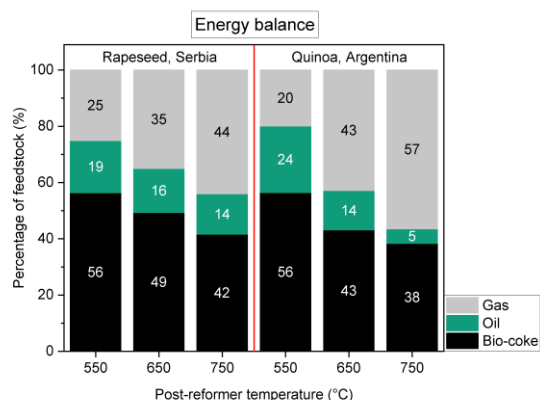

Figure 4: Energy balance of biomass conversion

3.2 Heavy metal distribution

Based on the product yields (Fig. 3) and the elemental concentrations in the corresponding products, the distribution of heavy metals in Rapeseed and Quinoa over different pyrolysis products at different temperatures is calculated according to the formulas in section 2.3 and further illustrated in Fig. 5 and Fig. 6.

The heavy metal distribution shows very ambiguous results for the tested feedstocks. For Rapeseed, most of the heavy metals (Cr, Cu, Zn and Ni) can be accumulated in the bio-coke for post-reformer temperatures of 550°C. With higher post-reformer temperatures, the amount of heavy metals in the bio-coke is decreasing. Cd and Pb, were mainly found in the gas and oil phases. For Quinoa, the results obtained for different post-reforming temperatures show a completely opposite trend. Here, the amount of heavy metals that can be trapped in the bio-coke fraction seems to rise at higher post-reforming temperatures. Similar to the Rapeseed trials, Cd was found mainly in the gas and oil phases.
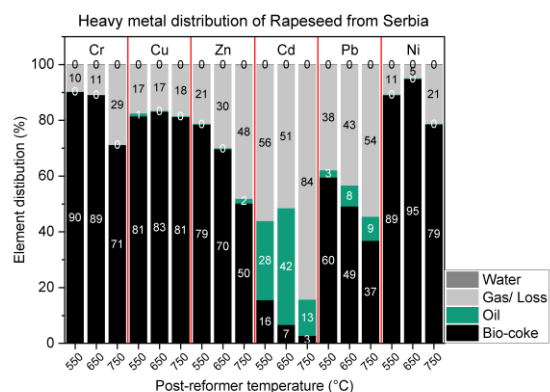

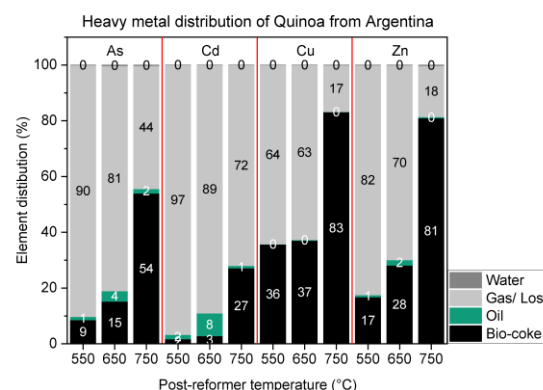**Figure 5:** Heavy metal distribution of Rapeseed from Serbia

Figure 6: Heavy metal distribution of Quinoa from Argentina

3.3 Gas analysis

The gases detected in the gas fraction (Table II) were H_2, CO, CO_2, and other non-condensable gases.

At the lowest reforming temperature (550°C) CO_2 is the main component for both feedstocks (35.1 vol% for Rapeseed and 40.4 vol% for Quinoa respectively).

At elevated reforming temperatures, the pyrolysis gas for both feedstocks consisted mainly of H_2 and CO. In particular, the increase in H_2 leads to a higher HHV. This is evident as the Quinoa syngas at 750°C contains a higher H_2 content (42 vol%) resulting in an improved HHV of 14.0 MJ kg^{-1}.

Table II: Rapeseed and Quinoa gas composition at different post-reformer temperatures (reactor temperature = 450°C). *Calculated by difference.

Post-reformer temperature	°C	Rapeseed, Serbia			Quinoa, Argentina		
		550	650	750	550	650	750
H_2	vol%	27.3	35.1	36.1	21.4	38.6	42.0
CO	vol%	10.0	15.0	23.4	11.5	14.6	22.1
CO_2	vol%	35.1	28.5	22.9	40.4	29.7	23.2
Other*	vol%	27.6	21.5	17.6	26.8	17.2	12.8
HHV	MJ kg^{-1}	7.5	11.5	13.0	9.9	12.0	14.0

3.4 Oil analysis

The bio-oil properties for the tested feedstocks at different reforming temperatures, after separation from the aqueous phase, are presented in Table III.

As the post-reformer temperature rises, an increase in carbon content and HHV is observed for Rapeseed. Quinoa also shows the highest carbon content and HHV at 750°C. Specifically, the HHV for Rapeseed increases from 30.7 MJ kg^{-1} at 550°C to 34.4 MJ kg^{-1} at 750°C, while for Quinoa, it increases from 36.1 MJ kg^{-1} at 550°C to 36.4 MJ kg^{-1} at 750°C.

The sulfur content of all Rapeseed and Quinoa bio-oils produced at different reforming temperatures is less than 0.6 wt%, which is below the 1.0 wt% limit for Low Sulfur Fuel Oil (LSFO) as specified by ISO 8217 (2017).

Table III: Rapeseed and Quinoa bio-oil at different post-reformer temperatures (reactor temperature = 450°C)

Post-reformer temperature	°C	Rapeseed, Serbia			Quinoa, Argentina		
		550	650	750	550	650	750
C	wt%	62.1	64.0	64.3	75.8	66.0	80.6
H	wt%	9.8	8.4	8.7	9.5	9.1	8.0
N	wt%	4.1	4.8	4.9	4.5	5.1	4.1
S	wt%	0.4	0.4	0.6	0.3	0.3	0.3
HHV	MJ kg^{-1}	30.7	33.1	34.4	36.1	31.5	36.4

4 CONCLUSION AND OUTLOOK

Within the scope of the EU-project "Phy2Climate", this study explored the feasibility of converting heavy metal contaminated biomass into high-quality energy carriers using the Thermo-Catalytic Reforming (TCR®) technology, focusing on two types of contaminated waste biomass: Rapeseed and Quinoa. Reforming temperatures were varied from 550°C to 750°C to assess their impact on product yield, quality, and heavy metal distribution.

The results demonstrated that increasing the post-reformer temperatures significantly influenced product yields and quality. Lower post-reformer temperatures favored the formation of bio-oil and bio-coke, while higher temperatures stimulated the production of pyrolysis gases, indicating a shift in the main energy carrier from bio-coke to gas. The distribution of heavy metals differed between rapeseed and quinoa. For Rapeseed, most of the heavy metals (Cr, Zn, Cd, Pb) accumulated in the bio-coke at the lowest reforming temperature of 550°C, with Cu and Ni concentrating at 650°C. In contrast, for Quinoa, heavy metals such as As, Cd, Cu, and Zn were mainly concentrated in the bio-coke at the highest reforming temperature of 750°C.

In context of the gas phase, higher reforming temperatures resulted in higher H$_2$ yields and increased HHV for both Rapeseed and Quinoa. In addition, bio-oil from both biomasses showed superior quality at the highest reforming temperature of 750°C. The sulfur content of the bio-oil from all experiments met the quality standards for low sulfur fuel oil (LSFO), as specified in ISO 8217 (2017).

The results obtained indicate that most of the heavy metals can be trapped in the bio-coke, however the effectiveness of the accumulation seems to depend on the biomass used and the form of the metal in it. Therefore, future research should be undertaken to get a better understanding about the chemical presence of the heavy metals within the biomass and how this influences their distribution within the conversion products. For volatile heavy metals such as cadmium or lead, strategies should be developed to effectively avoid the accumulation within the oil and gas phase. Furthermore, next to the sole conversion to high quality intermediates, individual upgrading strategies for the oil and gas phase should be deployed to produce drop-in biofuels according to international standards.

5 REFERENCES

[1] Neumann, J., Binder, S., Apfelbacher, A., Gasson, J. R., García, P. R., & Hornung, A. (2015). Production and characterization of a new quality pyrolysis oil, char and syngas from digestate–Introducing the thermo-catalytic reforming process. Journal of Analytical and Applied Pyrolysis, 113, 137-142.

[2] Jäger, N., Conti, R., Neumann, J., Apfelbacher, A., Daschner, R., Binder, S., & Hornung, A. (2016). Thermo-catalytic reforming of woody biomass. Energy & Fuels, 30(10), 7923-7929.

[3] Hornung, A., Jahangiri, H., Ouadi, M., Kick, C., Deinert, L., Meyer, B., ... & Eder, S. (2022). Thermo-Catalytic Reforming (TCR)–An important link between waste management and renewable fuels as part of the energy transition. Applications in Energy and Combustion Science, 12, 100088.

[4] Kick, Christopher, et al. "Development and Commissioning of an Innovative Biorefinery for the Conversion of Contaminated Biomass into High-quality Energy Carriers." (2023).

[5] Kick C., Kidikas, Z., Kasiulienė, A., Maletić, S., Zeremski, T., Rubežius, M., Eschen, M., & Ortner, M. (2025). Feasibility of using phytoremediation biomass for sustainable biofuel production via thermo-chemical reforming. Biofuels, Bioproducts and Biorefining. [Manuscript in press]

[6] Zeremski-Škorić, T., Sekulić, P., Maksimović, I., Šeremešić, S., Ninkov, J., Milić, S., & Vasin, J. (2010). Chelate-assisted phytoextraction: effect of EDTA and EDDS on copper uptake by Brassica napus L. Journal of the Serbian Chemical Society, 75(9), 1279-1289.

[7] Roqueiro, G., Guillen, L. F., Bárcena, N., Tornello, S., Ruiz Cortez, L. A., & Notario, L. (2020). Promoción del cultivo de quinua en los Valles Andinos y Centrales de San Juan como alternativa productiva y contribución a la seguridad alimentaria. EEA San Juan, INTA.

[8] Amjad, M., Iqbal, M. M., Abbas, G., Farooq, A. B. U., Naeem, M. A., Imran, M., ... & Jacobsen, S. E. (2022). Assessment of cadmium and lead tolerance potential of quinoa (Chenopodium quinoa Willd) and its implications for phytoremediation and human health. Environmental Geochemistry and Health, 1-14.

6 ACKNOWLEDGEMENTS