Business Use

A Wood-to-Wood Cascade Upcycling Valorisation Approach

WOOD2WOOD

» Deliverable 11.5

Assessment of dodecanol and validation of detergent formulations (version 1)

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or HADEA. Neither the European Union nor the granting authority can be held responsible for them.

WP No.	11
WP Title	Energy, Gas and Ashes valorisation
WP Leader	P&G
Due Date:	02/06/2025
Submission Date	30/06/2025
Authors	Sergio Barbarino, Diederik Van Houtte (P&G)
Contributing Partners	-
Status	Draft
Peer Reviewers	

PROJECT INFORMATION

GA Number	101091801
Project Full Title	Wood2Wood Project
Project Acronym	W2W
Funding Scheme	Horizon RIA
Start Date	01/01/2024
Duration	48 months
Coordinator	Dr. Angelos Amditis, Research and Development Director, ICCS
Project Website	In progress

Dissemination Level		
PU	Public	X
RE	Restricted to a group specified by the consortium	
CO	Confidential, only for members of the consortium (including the European Commission Services)	

REVISION AND HISTORY CHART

Version	Date	Author	Description of changes
0.1	10/06/2025	Sergio Barbarino	First draft
0.2	23/6/2025	Diederik Vanhoutte/Linsey Fuller	Second Draft
0.3	27/6/2025	Sergio Barbarino	Final Edit
2.0			Final submitted version
3.0			Revised submitted version (if required)

Legal Disclaimer

The opinion stated in this report reflects the opinion of the authors and not the opinion of the European Commission. All intellectual property rights are owned by Wood2Wood consortium members and are protected by the applicable laws. Reproduction is not authorized without prior written agreement. The commercial use of any information contained in this document may require a license from the owner of that information. While the information contained in the documents is believed to be accurate, the authors(s) or any other participant in the Wood2Wood consortium make no warranty of any kind with regard to this material including, but not limited to the implied warranties of merchantability and fitness for a particular purpose. Neither the Wood2Wood Consortium nor any of its members, their officers, employees or agents shall be responsible or liable in negligence or otherwise howsoever in respect of any inaccuracy or omission herein. Without derogating from the generality of the foregoing neither the Wood2Wood Consortium nor any of its members, their officers, employees or agents shall be liable for any direct or indirect or consequential loss or damage caused by or arising from any information advice or inaccuracy or omission herein.

1. TABLE OF CONTENTS

Glossary of acronyms 6
Executive summary 7
2. Objectives 8
3. Introduction 9
4. INTERMEDIATE PIVOT: UTILISING C16-C18 OIL PRODUCED BY KIVERDI 13
5. Conclusions 17
6. Annexes 18
7. References 18

Glossary of acronyms

Acronym	Extended Definition
W2W	Wood2Wood

List of Tables

Table 1. Suds Suppression Results

List of Figures

Figure 1. Synoptic Diagram of the Sulfation process via Falling Film Reactor

Figure 2. Suds References

Figure 3 Suds suppression results with Kiverdi Samples

EXECUTIVE SUMMARY

This deliverable presents the experimental outcomes of Tasks 11.5, which focus on a preliminary assessment of compatibility of the product obtained from Kiverdi in Task 11.4 (target Dodecanol from fermentation) with surfactants formulation and provide feedback to Kiverdi for process fine tuning in D11.5.

The second part of the deliverable (and also the resources associated) has been postponed to the next period (Task 11.5) as Kiverdi did not succeed in delivering neither the molecules nor the quantities necessary to accomplish this part (making of surfactants, and incorporating them in formulated products to be consumer tested)

Rather, given the different molecules delivered (a C16-18 fat) a pivot was suggested to initiate characterisation and labwork to test this material suitability in Dry Laundry detergency as fatty acids, specifically for suds and/or Calcium control. The Experimental plan produced mediocre performance in the context of suds suppression. Calcium control was not tested as this could not be expected as the fatty acids were delivered in the form of tryclicerides, i.e. still complexed with Glycerine. Therefore it is recommended to abandon this pivot and double down the efforts to achieve the sought for Dodecanol in the next phase of the project.

2. OBJECTIVES

The main objective of the task reported in this deliverable is to run a preliminary assessment of compatibility of dodecanol and exhausted cells from fermentation with surfactants formulation by performing different stress tests (such as Stability, Colour, Odour, Safety, etc..), to reveal eventual technical characteristics that could not be identified in the product assessment in T11.4 to provide feedback to KIV for process fine tuning D11.5.

While Kiverdi could only provide a fat containing higher (C16-C18) chains, this has still been tested for other potential applications, for example suds suppression and/or Calcium control in Dry Laundry detergents.

Part b) has been instead suspended until the next reporting period. This one consisted on using Kiverdi samples from TRL6 tests (kg scale) to progressively validate them into formulation of low impact detergents leveraging a micro falling film pilot reactor (TRL6) owned by P&G in Brussels centre that allows to convert fatty alcohols from exhausted cell biomass in ionic-surfactants for specific application in detergency (e.g., laundry detergents, fabric enhancers and dishwashing liquid). Small scale consumer exposure tests will be carried out for final validation of technical and safety performances.

In fact a first pivot was suggested that would have allowed to continue to part b) also with smaller samples from Kiverdi, using a mini chlorosulfonic reactor accessible to P&G staff, however this route as well had to be abandoned due to the different chemical composition of the material obtained by Kiverdi Fermentation process.

3. INTRODUCTION

Surfactancy describes the ability of certain molecules, known as surfactants (**surf**ace-**act**ive **a**ge**nts**), to modify the properties of interfaces, particularly between immiscible phases like oil and water or air and water. This remarkable ability stems from their amphiphilic nature: surfactant molecules possess both a hydrophilic (water-loving) head group and a lipophilic (oil-loving) tail. This dual affinity allows them to preferentially adsorb at interfaces, reducing interfacial tension and facilitating the mixing or dispersion of otherwise incompatible substances.

Surfactants are core materials in modern detergents. Anionic surfactants more specifically are particularly prominent due to their excellent detergency, foaming, and emulsifying properties. A key step in the synthesis of many anionic surfactants, particularly those with linear alkyl chains, is the **sulfation process**.

Sulfation involves the introduction of a sulfate group (−OSO_3H or its salt form, −OSO_3−) onto an organic molecule. This process is distinct from sulfonation, which involves the direct attachment of a sulfonate group (−SO_3H or −SO_3−) directly to a carbon atom. In the context of surfactants, sulfation typically involves the reaction of an alcohol with a sulfating agent, leading to the formation of an alkyl sulfate. The sulfate group, being highly polar and capable of ionization, serves as the hydrophilic head group, while the alkyl chain forms the lipophilic tail.

Με σχόλια [JG1]: I cannot see the symbol between O3 and H

Με σχόλια [JG2]: same

Με σχόλια [JG3]: same

More specifically sulfation processes are used for the synthesis of linear chain surfactants, particularly those derived from dodecanol. Dodecanol, also known as lauryl alcohol, is a straight-chain fatty alcohol with 12 carbon atoms ($C_{12}H_{25}OH$). It is a common precursor for the synthesis of various surfactants due to its readily available linear alkyl chain, which provides an optimal balance of hydrophobicity and biodegradability for many applications.

The sulfation of dodecanol typically proceeds via reaction with a strong sulfating agent. The most common and industrially significant sulfating agents for this purpose include (Roberts, 1998):

1. **Sulfur Trioxide (SO_3):** This is perhaps the most widely used and efficient sulfating agent. The reaction is highly exothermic and requires careful control of temperature to prevent side reactions and degradation of the product. The reaction can be represented as:

   $R\text{-}OH + SO_3 \rightarrow R\text{-}OSO_3H$ where R represents the dodecyl group ($C_{12}H_{25}$).

2. **Chlorosulfonic Acid ($ClSO_3H$):** This is another effective sulfating agent, particularly useful when anhydrous conditions are preferred. The reaction generates hydrogen chloride gas as a byproduct, which needs to be handled appropriately.

   $R\text{-}OH + ClSO_3H \rightarrow R\text{-}OSO_3H + HCl$

3. **Sulfuric Acid (H_2SO_4):** While less reactive than SO_3 or $ClSO_3H$, concentrated sulfuric acid can also be used for sulfation, especially for less sensitive alcohols. However, it often requires higher temperatures and can lead to side reactions like ether formation or dehydration if not carefully controlled. $R\text{-}OH + H_2SO_4 \rightleftharpoons R\text{-}OSO_3H + H_2O$

Following the sulfation step, the resulting alkyl sulfuric acid ($R\text{-}OSO_3H$) is typically neutralized with a base, commonly sodium hydroxide (NaOH), to form the corresponding salt, which is the actual surfactant. For dodecanol, this yields **sodium dodecyl sulfate (SDS)**, also known as sodium lauryl sulfate (SLS): $C_{12}H_{25}OSO_3H+NaOH \rightarrow C_{12}H_{25}OSO_3Na+O$

Sodium dodecyl sulfate is a prime example of a linear chain anionic surfactant. Its precisely engineered structure—a linear C12 hydrophobic tail attached to a highly polar sulfate head group—confers excellent surface-active properties. It readily forms micelles above its critical micelle concentration (CMC), effectively solubilizing greases and oils, and is renowned for its high foaming capabilities. These properties make it a staple ingredient in a vast array of cleaning and personal care products.

P&G runs a small scale Falling film reactor in its Brussels Innovation Center that allows us to study the steady state sulfation via the route described under 1) with small quantities (Kg) of Alcohols. A schematic of the Raw materials treatment and the sulfation process in these reactors is presented in the figure below

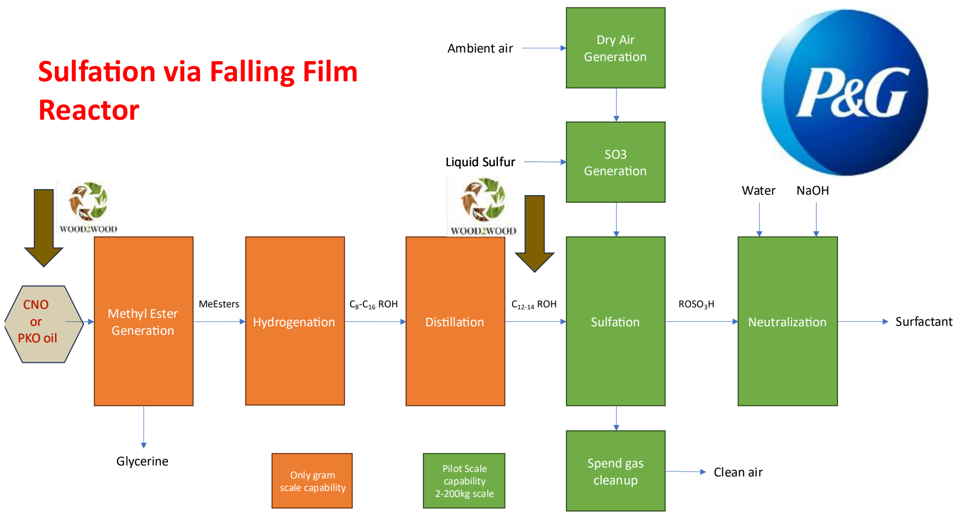


Figure 1

P&G has also access to a Chlorosulfonic reactor that can run a batch sulphation described above under 2) with very small quantities (grams) of material.

Dodecanol (lauryl alcohol) for surfactant production is normally sourced from either Oleochemical or Petrochemical routes.

Natural (Oleochemical) Sources

The primary natural sources of dodecanol are vegetable oils, specifically:

- **Palm Kernel Oil:** This is currently the most significant source globally. Palm kernel oil is derived from the kernel (seed) of the oil palm fruit.
- **Coconut Oil:** Another major source, coconut oil is extracted from the meat of mature coconuts.

Both palm kernel oil and coconut oil are rich in lauric acid (a C_{12} fatty acid), which is the precursor to dodecanol. The process of obtaining dodecanol from these natural oils involves several steps:

1. **Hydrolysis/Transesterification:** The triglycerides (fats) in the oils are first broken down into fatty acids and glycerol through hydrolysis, or into fatty acid methyl esters (FAMEs) through transesterification with methanol.
2. **Fractionation:** The mixture of fatty acids or FAMEs is then typically fractionated (separated) to isolate the desired C_{12} fraction, which is predominantly lauric acid or its methyl ester.
3. **Hydrogenation (Reduction):** The isolated lauric acid or lauric acid methyl ester is then subjected to high-pressure hydrogenation. This process adds hydrogen across the carbonyl group (the C=O double bond) of the fatty acid or ester, reducing it to a fatty alcohol.
   - For lauric acid: $C_{11}H_{23}COOH+2H_2 \rightarrow C_{11}H_{23}CH_2OH+H_2O$
   - For methyl laurate: $C_{11}H_{23}COOCH_3+2H_2 \rightarrow C_{11}H_{23}CH_2OH+CH_3OH$

This oleochemical route yields "natural" fatty alcohols that are generally linear and have an even number of carbon atoms, reflecting the composition of the source triglycerides.

Synthetic (Petrochemical) Sources

While natural sources dominate, dodecanol can also be produced synthetically from petroleum-derived feedstocks. The main synthetic pathways include:

- **Ziegler Process (or Alfol Process):** This process involves the oligomerization of ethylene to produce long-chain alpha-olefins, followed by oxidation and hydrolysis to yield fatty alcohols. This process allows for precise control over chain length distribution.

  $nCH_2{=}CH_2 \rightarrow R{-}CH{=}CH_2 \rightarrow R{-}CH_2OH$

- **Oxo/Modified oxo Process (Hydroformylation):** This process involves the hydroformylation of alpha-olefins (obtained from cracking petroleum fractions) with carbon monoxide and hydrogen to form aldehydes, which are then hydrogenated to alcohols.

  $R{-}CH{=}CH_2+CO+H_2 \rightarrow R{-}CH_2CH_2CH_2OH$

  While the oxo process can produce dodecanol, it often yields a mixture of linear and branched alcohols, depending on the olefin feedstock.

Synthetic routes offer independence from agricultural commodity price fluctuations and land use concerns, but they rely on finite fossil resources and have a higher carbon footprint compared to well-managed natural sources.

Sustainability Considerations in Sourcing Dodecanol

The sourcing of dodecanol from petrochemical sources is nonrenewable but also natural sources have attracted concerns related to palm oil production:

- **Deforestation and Biodiversity Loss:** The expansion of oil palm plantations, particularly in Southeast Asia, has historically been linked to deforestation, habitat destruction, and loss of biodiversity (e.g., orangutans).
- **Greenhouse Gas Emissions:** Deforestation and the drainage of peatlands for palm oil cultivation release large amounts of greenhouse gases.
- **Social Impacts:** There have been concerns about labor practices, land rights, and displacement of local communities in some palm oil-producing regions.

Several attempts have been documented of alternative sources, even if none of them has so far being scaled successfully. For example: algae oil, jatropha, genetically engineered oilseed crops, Soldiers ants' larvae etc.

Within the context of the W2W project an alternative supply chain derived from wood waste is being tested:

Bio-based Dodecanol (from Fermentation): An emerging area is the microbial production of fatty alcohols, including dodecanol, using biotechnology. Engineered microorganisms (e.g., *E. coli* or yeast) can be fed with sugars or other biomass-derived feedstocks (in our case syngas derived from Wood waste) to produce fatty alcohols through fermentation. This offers a potentially highly sustainable route, minimizing land use impact.

The main outcomes at the end of the project will be the Techno-economic validation of the new supply chain studied in the W2W project via Wood, Syngas biochemical synthesis of dodecanol and sulfation. It will also include a small base consumer test of the final detergent products.

The following sections of the deliverable will detail the experimental approach, results, and analysis supporting these goals.

4. INTERMEDIATE PIVOT: UTILISING C16-C18 OIL PRODUCED BY KIVERDI

3.1. INTRODUCTION

Suds suppressors, commonly known as anti-foaming agents or defoamers, are essential components in the formulation of laundry detergents, particularly in dry laundry products. Their primary function is to control foam levels during the washing process, ensuring optimal performance of washing machines and enhancing overall cleaning efficacy.

The study investigates the potential of lipids derived from microbial processes to function as suds suppressors in laundry detergent formulations. Specifically, three lipid samples, primarily composed of C16 fatty acids, were assessed for their foam reduction capabilities in comparison to a commercial antifoam agent.

Initially we hoped to test the materials delivered also in the context of Calcium control, but this was abandoned as the fatty acids were still complexed with Glycerine (as Tryclicerides) as therefore not suitable at all for this purpose.

Importance of Antifoam Agents in Dry Laundry Products

1. **Operational Efficiency**

   Dry laundry detergents, especially those designed for high-efficiency (HE) washing machines, require precise control of foam levels. HE machines utilize significantly less water than traditional models, making it crucial to avoid excessive sudsing, which can lead to overflow, mechanical issues, and inefficient rinsing of fabrics. Antifoam agents maintain the appropriate balance of foam, ensuring that washing machines operate smoothly while delivering good cleaning performance.

2. **Cleaning Performance**

   Effective cleaning relies on the ability of detergents to penetrate fabrics and remove dirt. Excessive foam can obstruct this process by creating a barrier between the detergent and the fabric, thereby limiting the product's effectiveness. By controlling foam levels, antifoam agents enhance the overall cleaning performance of laundry products, ensuring that dirt and stains are effectively removed.

3. **Consumer Experience**

   Consumers expect laundry products to perform efficiently without excessive foaming, which can lead to spills and mess during the washing cycle. Products marketed as low-sudsing tend to enhance user satisfaction, making suds suppressors a critical element in product formulation.

Types of Suds Suppressors

1. **Silicone-Based Compounds**

- **Mechanism**: Silicone compounds effectively suppress suds due to their ability to spread across foam surfaces, destabilizing foam and reducing its formation.
- **Example**: Zeolites are widely used in both household and industrial applications for reliable foam control.

2. **Hydrophobic Powders**
   - **Mechanism**: These powders absorb moisture and disrupt foam formation by adhering to the surfaces of bubbles, effectively reducing foam.
   - **Example**: Hydrophobic silica is commonly employed in industrial applications to control foam and improve product stability.
3. **Surfactants with Anti-Foaming Properties**
   - **Mechanism**: Certain surfactants are designed to exhibit both cleaning and foam control properties, allowing for dual action in formulations.
   - **Example**: Non-ionic surfactants, such as ethylene and propylene oxide adducts of fatty alcohols (block copolymers), exhibit antifoam properties alongside cleaning capabilities. These surfactants provide mild cleaning action while managing suds.

Alternative Suds Suppressors

1. **Fatty Acids**
   - **Mechanism**: Fatty acids can function as surfactants due to their amphiphilic nature, typically suppressing foam rather than promoting it.
   - **Examples**: Stearic acid, found in personal care and cleaning products, influences foam behavior but is not an effective standalone suds suppressor. Oleic acid also contributes to the surfactant balance but may not effectively reduce suds.
2. **Triglycerides**
   - **Mechanism**: Triglycerides, the primary form of lipids, consist of glycerol bonded to three fatty acid chains. Their structure provides unique properties that can influence cleaning formulations. Triglycerides can act as surfactants due to their amphiphilic nature, featuring hydrophobic fatty acid tails and a hydrophilic glycerol backbone. Shorter-chain fatty acids, such as those found in coconut oil, are more soluble in water, enhancing emulsifying capabilities and cleaning efficacy. Conversely, triglycerides derived from longer-chain fatty acids (e.g., palmitic or stearic acid) may exhibit reduced solubility, complicating their incorporation into formulations and leading to challenges with foam control and residue on fabrics.
   - **Applications in Formulations**: Triglycerides may be explored as multifunctional ingredients in formulations targeting markets with a lower carbon footprint. Their use can provide moisturizing benefits to fabrics while serving as antifoam agents; however, careful formulation is necessary to ensure they remain effectively solubilized within the product.

3.2. METHODOLOGY

- This section outlines the approach taken to investigate the use of C16-C18 oil produced by Kiverdi, detailing the experimental design and specific methodologies employed.

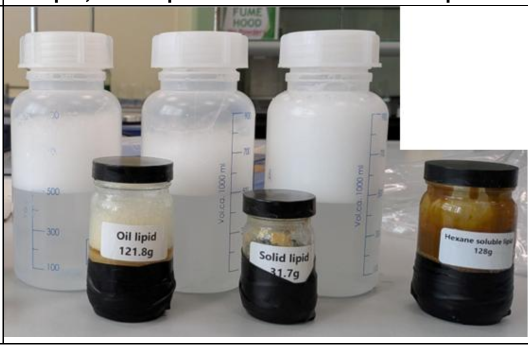
  The experimental setup involved developing a method to assess the suitability of C16-C18 oil as a calcium control agent in dry laundry detergents. A series of tests were conducted to evaluate its effectiveness in reducing foam and enhancing cleaning performance. Adjustments were made to the method based on preliminary results, addressing challenges such as solubility and compatibility with other detergent components.

3.2.1. Design of Experiments

- **Lipid Samples**: Three lipid samples were analyzed:
  - **Sample 1**: Hexane Soluble Lipid
  - **Sample 2**: Oil Lipid
  - **Sample 3**: Solid Lipid
- **Experimental Setup**: Each lipid sample was tested in an existing commercial laundry detergent formulation, replacing the incumbent silicone-based antifoam agent on an equal mass basis. Foam suppression was measured using a standard foam reduction protocol, comparing the experimental samples against the reference formulation.
- **Pre-treatment of the Sample**: The C16-C18 oil was subjected to pre-treatment processes to enhance its properties for use in laundry detergents. These processes included filtration and the removal of impurities, which are crucial for ensuring the quality of the final product.

3.2.2 Results

	Oil Lipid	**Solid Lipid**	**Hexane Soluble Lipid**
Foam reduction vs. reference	12.5%	25%	0%
Observation	Some suppression observed	Moderate suppression observed	No suppression observed
	Partial solubility or interaction with foam structures	Likely physical interaction with foam surfaces	Poor solubility and interaction with aqueous foam

Blank (left) and Reference (Right)	Kiverdi Samples - From left to right Oil Lipid, Solid Lipid and Hexane Soluble sample
	

Suitability as Calcium Control Agent in Dry Laundry Detergents

- **Experimental Evaluation of Kiverdi Samples as Suds Suppressors**: The evaluation of Kiverdi lipids as suds suppressors showed varying performance:
  - **Oil Lipid**: 12.5% foam reduction
  - **Solid Lipid**: 25% foam reduction
  - **Hexane Soluble Lipid**: 0% foam reduction

Observations indicated that the Oil Lipid and Solid Lipid samples exhibited some foam suppression, while the Hexane Soluble Lipid demonstrated no foam suppression, likely due to its hydrophobic nature and poor solubility in the aqueous environment of the wash solution.

3.3. DISCUSSION OF RESULTS

The experimental evaluation of Kiverdi lipids as suds suppressors shows poor to suboptimal performance compared to the reference antifoam agent. Several factors may contribute to these results:

- **Limited Solubility**: The hexane-soluble lipid displayed no foam suppression, likely due to its hydrophobic nature, resulting in poor dispersion in the aqueous environment of the wash solution. This limited its interaction with foam bubbles, a critical factor for effective foam suppression.
- **Inadequate Formulation Design**: The existing detergent formulation is likely not optimized for lipid-based antifoam agents. Traditional suppressors are often designed to work synergistically with specific surfactants and emulsifiers, which may not be compatible with the tested lipids.
- **Physical State and Interaction**: The oil and solid lipids showed moderate foam suppression, indicating that physical state and lipid-surfactant interactions play a role. However, the lack of significant suppression suggests that these lipids may not adequately destabilize foam, possibly due to insufficient surface activity or interaction with the detergent matrix.

- **Chain Length and Saturation Effects**: The C16 fatty acid composition might not provide the optimal balance of hydrophobic and hydrophilic properties required for effective suds suppression. Variations in chain length and saturation could alter solubility and interfacial activity, impacting foam control capabilities.

5. CONCLUSIONS

The challenges faced in using the Kiverdi lipids as suds suppressors—pivoting from the original project objective of producing dodecanol—are partly due to the late-stage receipt of lipid samples from Kiverdi, stemming from the experimental nature of their work. This timing limited the ability to conduct extensive testing and optimization within this reporting period by Procter & Gamble.

As we move forward, the focus of Kiverdi will return to investigating the initial goals of the project, specifically the production and application of dodecanol. This compound can then be further processed into anionic surfactants to be tested in formulations for efficacy.

Only Minimal resources were employed to achieve these conclusions, given the limited time frame and the necessity of the pivot due to the failure to produce the sought for Dodecanol. This will allow to double down on efforts in the second phase of the project.

6. Annexes

None

7. References

Roberts, D. W., 1998. Sulfation Technology for Anionic Surfactant Manufature. *Organic Process Research & Development,* 2(3), pp. 194-202.

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or HADEA. Neither the European Union nor the granting authority can be held responsible for them.

WOOD2WOOD

Disclaimer: Content reflects only the authors' view and European Commission is not responsible for any use that may be made of the information it contains.