Producing biofuels – meeting demands while overcoming obstacles
Focus on R&D activities

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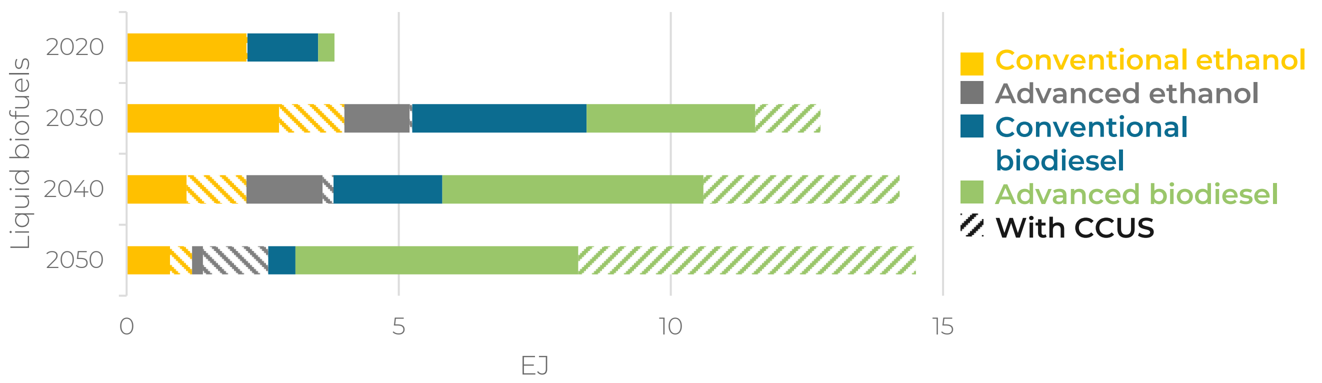
Biofuels in Transport: Production Scenario and Global Demand

In the IEA's NZE to 2050 scenario, it is noted that:
Liquid biofuels: upward trend in consumption increasing by about four times between 2020 and 2050
Biogas and biomethane planned to expand by about six times between 2020 and 2050.

Global Biofuel Production by type and Technologies in the NZE

IEA

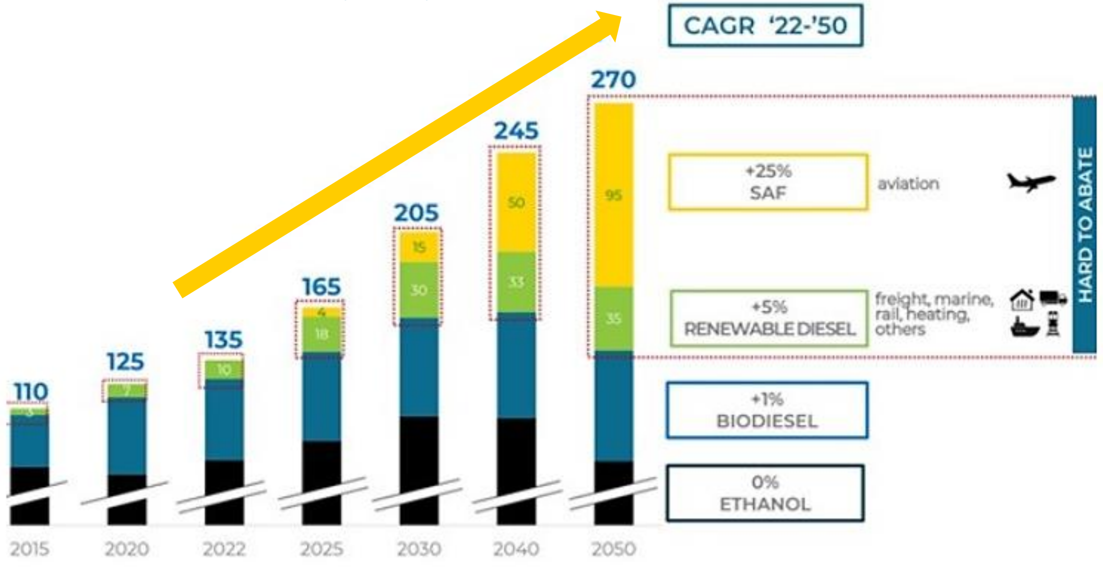


In the global demand scenario:

SAF demand up +25% from 2022 to 2050

HVO: demand expected to increase slightly but the need to decarbonize hard-to-abate sectors could lead to a larger increase

Global Biofuel Demand (MTPA)



BioRefineries for the production of HVO and SAF

Eni BioRefineries System

ON GOING PROJECTS

- Livorno (Italy), Malaysia, South Korea
- Chalmette (Louisiana, USA): operating biorefinery, JV with PBF Energy

VENICE BIO.REFINERY (2014)

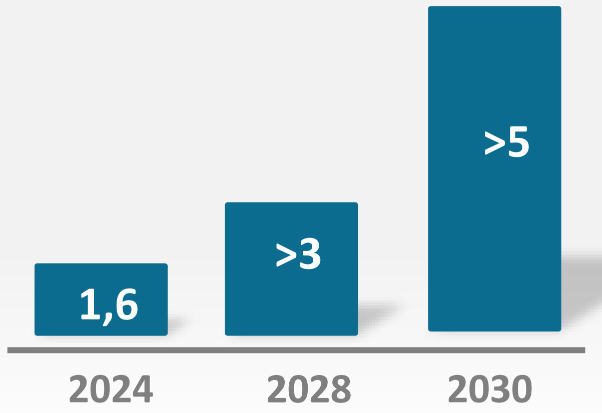
- **Capacity:** 0.4 Mt/y
- **Products:** HVO-Diesel, HVO-Naphtha and LPG

GELA BIO.REFINERY (2019)

- **Capacity:** 0.7 Mt/y
- **Products:** HVO-Diesel, HVO-Naphtha and HVO-LPG

PALM OIL FREE since 4Q2022

EXPANSION STRATEGY – ORGANIC GROWTH (Mln t/y)



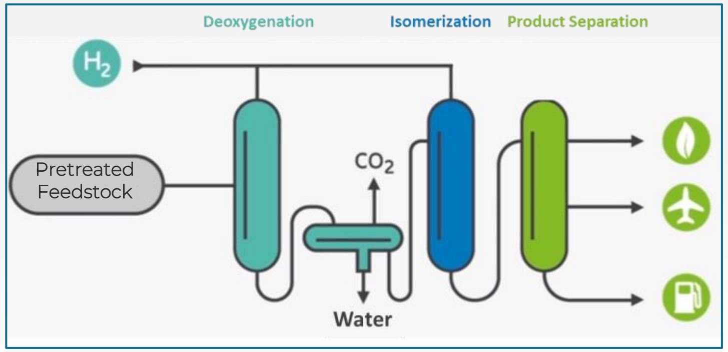
From sustainable feedstock to biofuels thanks to BioRefinery

FEEDSTOCK

- Energy crops
- Oleaginous seeds
- Waste & Residues

PROCESS

Eni and UOP developed the ECOFINING™ Process



BIOFUELS

- HVO - LPG
- HVO - NAPHTHA
- HVO- JET
  ENI BIOJET
- HVO-DIESEL
  HVOlution

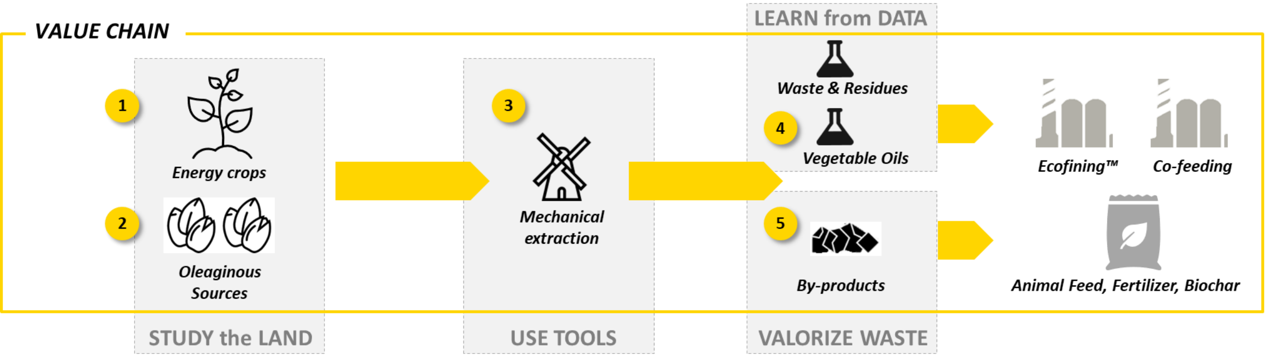
Eni strategy for decarbonization: the vertical integration model

Biofuels will play a central role in achieving Eni's decarbonization mission by 2050.
In parallel with the supply of Bio feedstocks from the market, in particular Waste & Residues, for our Bio-Refineries, Eni is working on developing an innovative vertical integration model, from oilseed processing plants (agri-hubs) to biorefineries.

To ensure, through crops integrated with the supply chain, **the supply of biorefineries.**

Stabilize and reduce the risk exposure, for a significant part, of the necessary **feedstock volumes,** in a volatile scenario both in terms of prices and **raw material availability**

Control of the entire industrial chain, **support and monitoring** of farmers' activities**, disseminating agricultural *best practices*** in the various stages of cultivation.



Agri feedstock

Sustainable raw materials: NO competition with food value chain

NOVEL VEGETABLE OILS

CASTOR DEGRADED LAND
non-food crop, drought resistant, suitable for inter-cropping, high oil content, sinergies with carbon farming

COVER CROPS
intermediate crops after primary production cycle: camelina, brassica c, sufflower, other.

AGRO-FORESTRY
Trees planted by farmers in agricultural areas, in synergy with carbon offset program. Stimulate land regeneration

RESIDUES

FOOD AND AGRO INDUSTRIES
residual biomass from food processing industries, and ginneries; circular economy and industrial symbiosis

FORESTRY RESIDUES
residual oilseed from plantations or spontaneous trees; synergy with cooperatives and large agribusiness

OTHER BIO FEEDSTOCK
residues from animal husbandry, fishing and other agro-industrial processing; UCO and organic wastes

Low ILUC Feedstock

Land not in competition with the food chain

NO FOOD CROP ON SEVERELY DEGRADED LAND

LOW SOIL ORGANIC CARBON

HIGH EROSION

COVER CROP AND INTERCROP

Energy crops in rotation or cultivated in the same field and at the same time with food crops

New feedstocks in ANNEX IX

IDENTIFICATION OF CROPLAND

GIS analysis:

- time series of LU data from ESA (European Space Agency)
- national, regional and local scale analysis
- Pilot on Horizon BIKE Project
- Collaborations for advanced digital tools

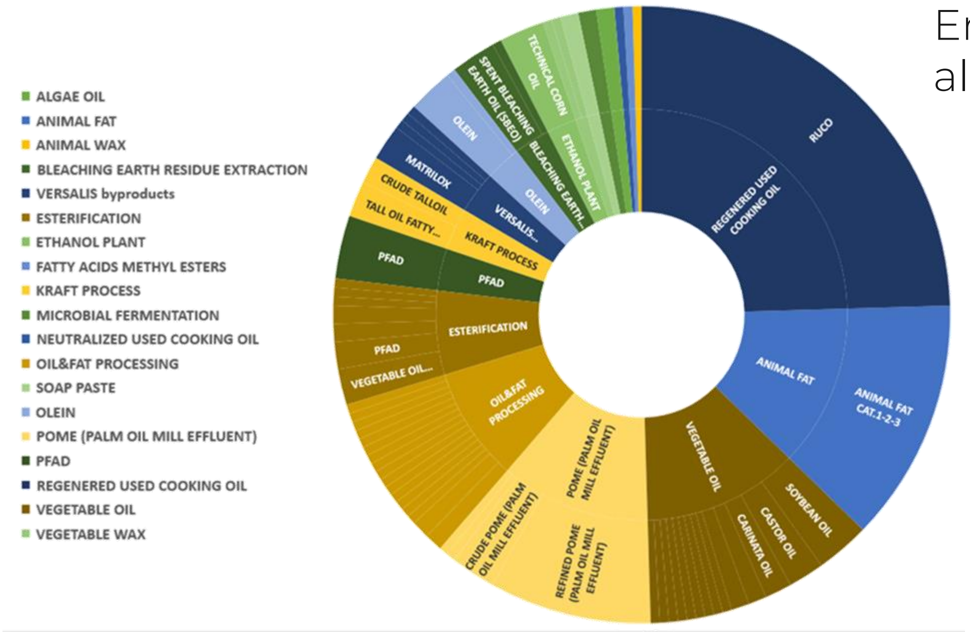
IDENTIFICATION OF SEVERELY DEGRADED LAND

GIS analysis of soil data (ISRIC – Soil organic Carbon)

Vegetable oils: Eni Biofeedstocks Database

Vegetable Oils valorization

Ample and flexible feedstocks for Ecofining™ technology



Eni biofeedstocks database allows to:

- **Optimize** the processing on the Bio-Cycle, **estimating and anticipating critical issues**
- **Assess** for the available feedstocks (**R&D**), supporting the decision makers to implement a feedstock diversification strategy providing **elements for evaluations**.

Biocrude assay database with more than 480 characterized feedstocks

Bio-Fuels: HVO-Diesel

HVO-DIESEL: HVOlution

- 100% from Renewable feedstock
- Bio-fuels with a complete hydrocarbon nature (free of oxygen) consisting of a mixture of stable and non-hygroscopic paraffins
- It is free of aromatic, polyaromatics compound and sulphur, the most impacting compounds from an environmental point of view
- It has a high cetane number with a good cold properties and excellent engine performance
- ALREADY AVAILABLE IN +1000 EniLive SERVICE STATIONS

1 ROAD TRANSPORT

- Eni Diesel+ is a premium Diesel formulation with 15% HVO, currently distributed in Eni service stations as diesel+
- HVOlution is 100% HVO, currently distributed in +1000 EniLive service stations as HVOlution

2 VEHICLES FOR HEAVY TRANSPORT: 100% HVOlution

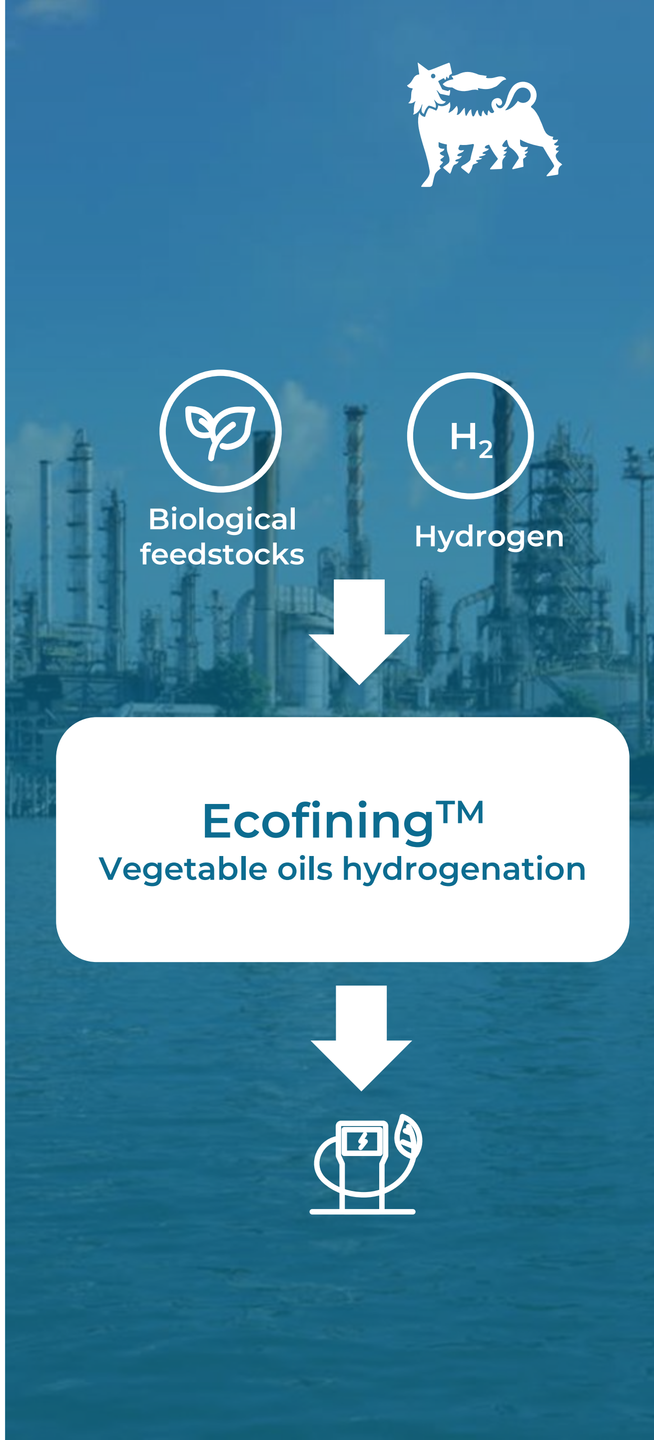
- Eni is promoting many collaborations with heavy transport vehicle manufacturers to demonstrate the concrete reduction of emissions with 100% of HVOlution in the sector that is considered Hard To Abate.

3 NAVY TRANSPORT

- Eni promotes collaboration with the actors of the maritime sector to spread the diffusion of HVOlution

4 AVIATION: SAF

- Eni Biojet is the SAF (Sustainable Aviation Fuel) which contains 100% biogenic component and is suitable for use in mixtures with conventional jet up to 50%.



Eni R&D

Oil seed crops | LOW ILUC

Camelina sativa

Seed yield: 500-2000 kg/ha
Oil content: 30–49%
Oil yield: ~320 kg/ha

Brassica Juncea

Seed yield:1000-3000 kg/ha
Oil content: 36-49%
Oil yield: ~910 kg/ha

Brassica Carinata

Seed yield: 1500-2700 kg/ha
Oil content: ~40%
Oil yield: ~600 kg/ha

Carthamus tinctorius

Seed yield: 2000-4000 kg/ha
Oil content: ~35%
Oil yield: ~ 992 kg/ha

Hevea Brasiliensis

Seed yield: 800-1200 kg/ha
Oil content: 38–46%
Oil yield: ~400 kg/ha

Selection criteria:

- Yield per hectare
- Geographical distribution of the plant
- Oil content (% wt)
- Composition of the oil
- Possible toxicity of the seed and cake
- Commercial use of the cake (fertilizers, feed, biochar production)

- Eni stopped the supply of **palm oil** to its Venice and Gela bio-refineries **as early as October 2022**
- Recruitment of **new potential** oil seed crops

Oleaginous seeds laboratory

Pretreatment

❑ Shelling

Seeds

Shell

Kernel

❑ Grindig

Seeds

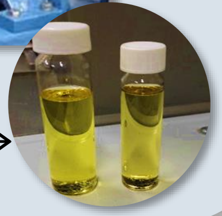
Oil extraction

❑ Solvent extraction:
- *Oil quantity determination / theoretical yield*

❑ Mechanical extraction
- *Technical feasibility*
- *Δyield: Mechanical vs Solvent*

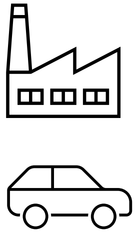
Cake

Oil

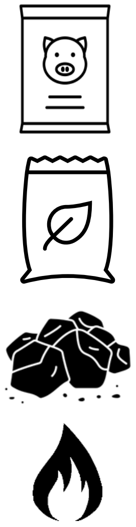


Characterization

❑ Oil
- *Chemical-physical characterization*
- *Comparison with standard biorefinery feedstock*
- *Evaluate the compatibility of extracted oil for biorefineries*
- *Identification of critical issues*
- *The first GO/ NO GO*
- *Screening tests*



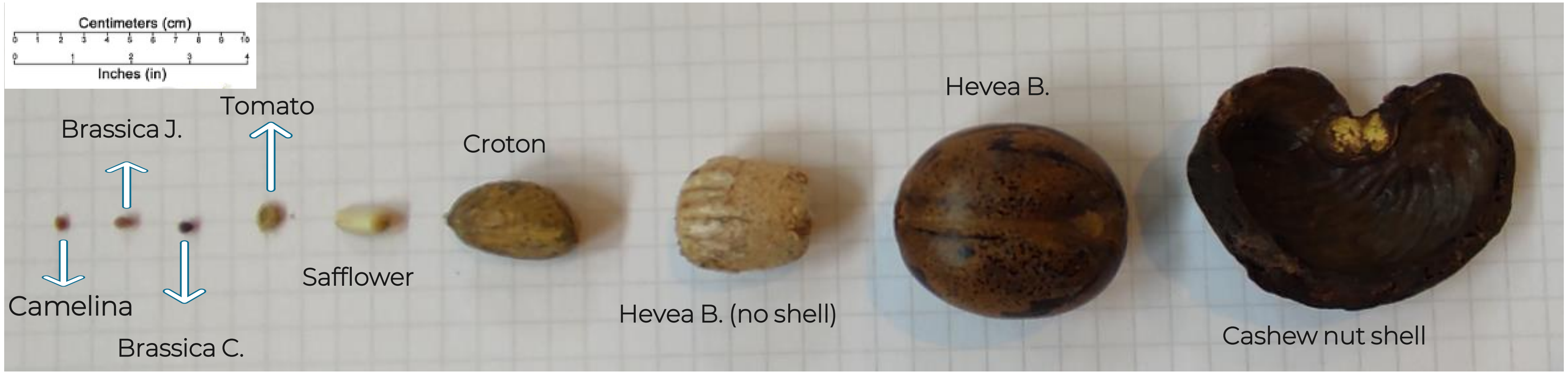
❑ Cake
- Chemical-physical characterization:
  - Residual oil
  - Contaminants
  - Crude Protein
  - Fibers (NDF, ADF, ADL)
  - Starch
  - Ash
  - Macroelements/ Microelements



Different seeds

- ❑ Camelina Sativa
- ❑ Brassica Juncea
- ❑ Brassica Carinata
- ❑ Tomato
- ❑ Croton
- ❑ Safflower
- ❑ Hevea Brasiliensis
- ❑ Peanuts
- ❑ Macadamia
- ❑ Carthamus Tinctorius

Different dimensions of some oleaginous seeds and residues



Mechanical extraction vs. Chemical extraction: Vegetable Oils and By-products

Mechanical extraction

The technology for the mechanical extraction of oil from seeds is known both to produce edible oil and biodiesel. Mechanical extraction R&D activities aim at assessing the effective yield of biofeedstocks, optimizing processes and increasing yields.

Screw machine (2-5 kg/h)

Screw machine (up to 20 kg/h)

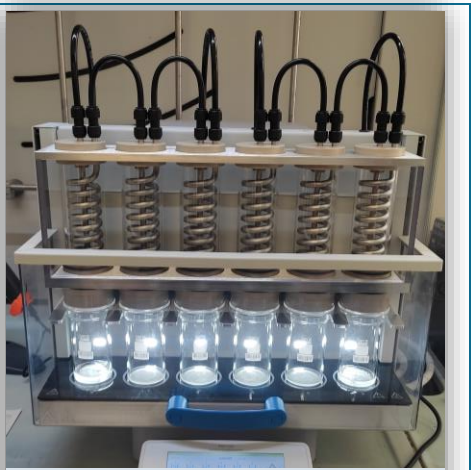
Press machine (~0.6 kg/batch)

Experiments to identify optimal operating parameters for oil extraction at the highest yield possible by means of mechanical treatment only → <u>gap reduction</u> with solvent extraction.

Chemical extraction

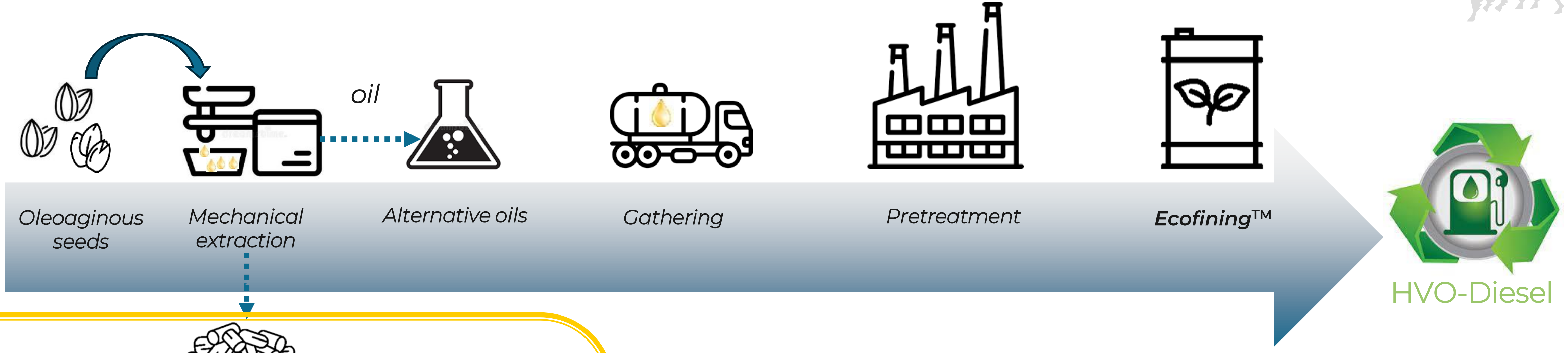
Solvent extraction is used to determine the oil content in the seed: it is more efficient than mechanical pressing but energy intensive.

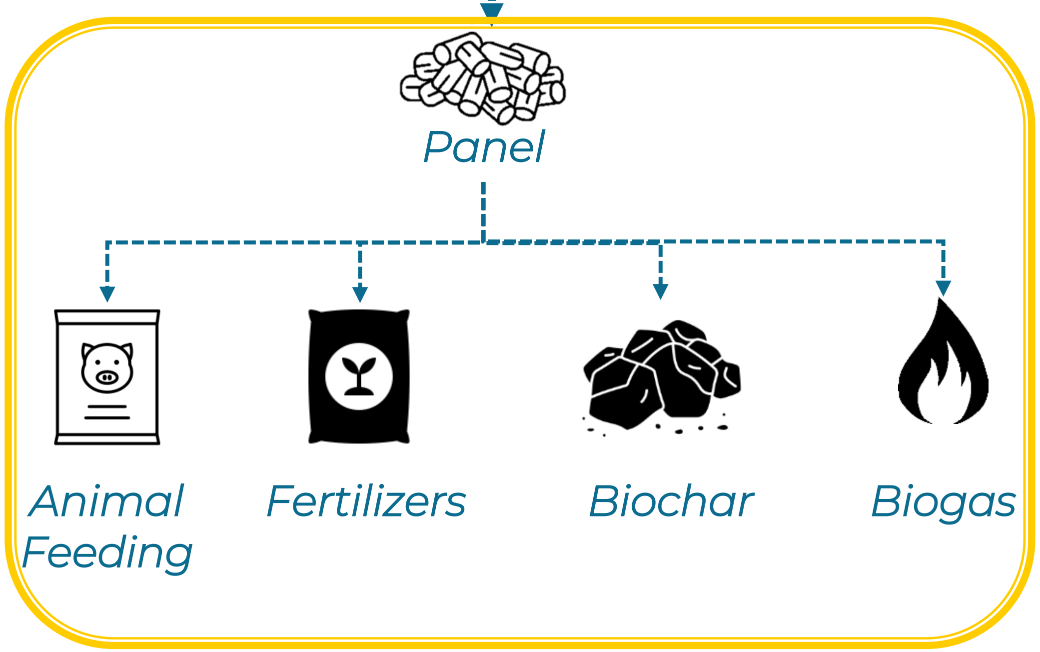
Soxhlet + Rotavapor



Automatic extractor– SER 158

Value chain & Oil-seed cakes valorization





- ❑ Increase the portfolio of bio-feedstocks in Biorefineries using biomass from AGRI supply chain
- ❑ Increase the environmental and economic sustainability of the supply chain by **valorizing all agricultural production residues and waste**
- ❑ Decarbonization of HVO supply chain

Oil-seed cakes valorisation

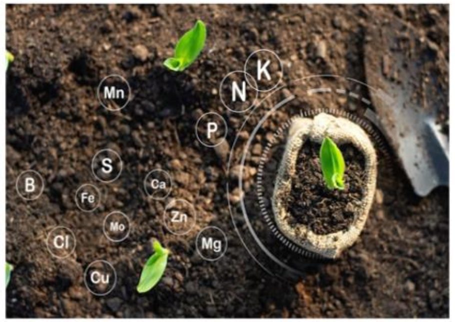
Animal feeding

Dietary supplemental protein and carbohydrates source

Rich in antioxidants, minerals, vitamins

Suitable for organic farms

Fertilizers



Nitrogen supplying (N is now very expensive)

Soil organic matter increase

Reducing N_2O emissions

Biochar

High Carbon content

Moisture < 10%

Low ash content

Biogas/Biomethane

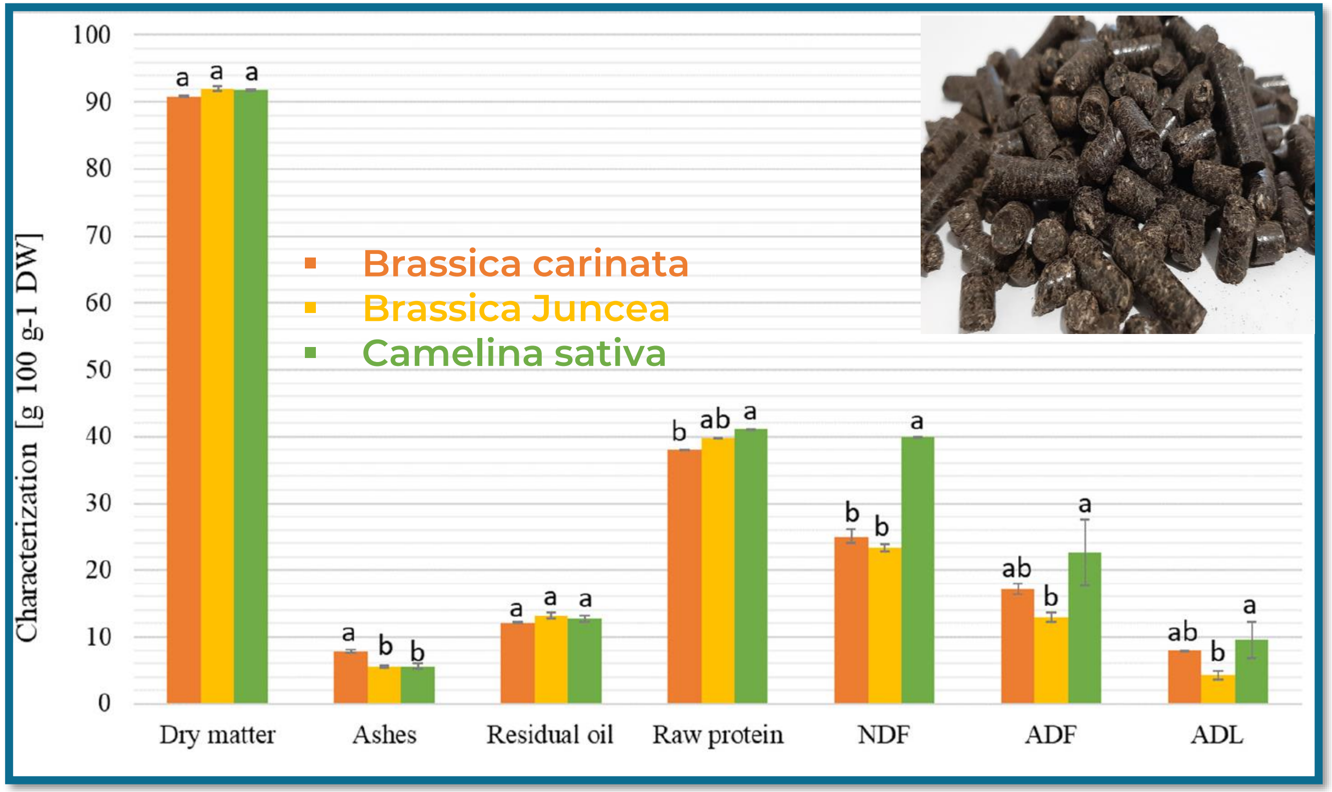
Heat/Electricity

Biofuel

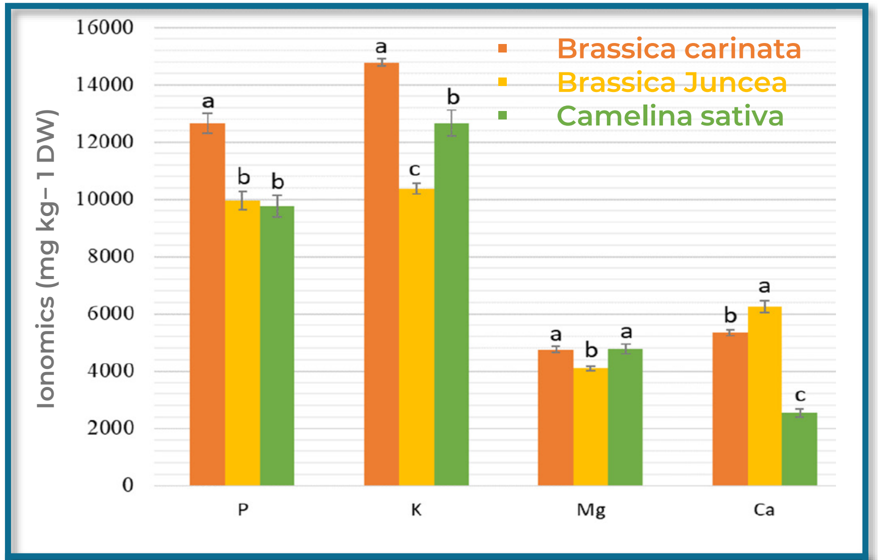
Good preliminary results on Hevea cake

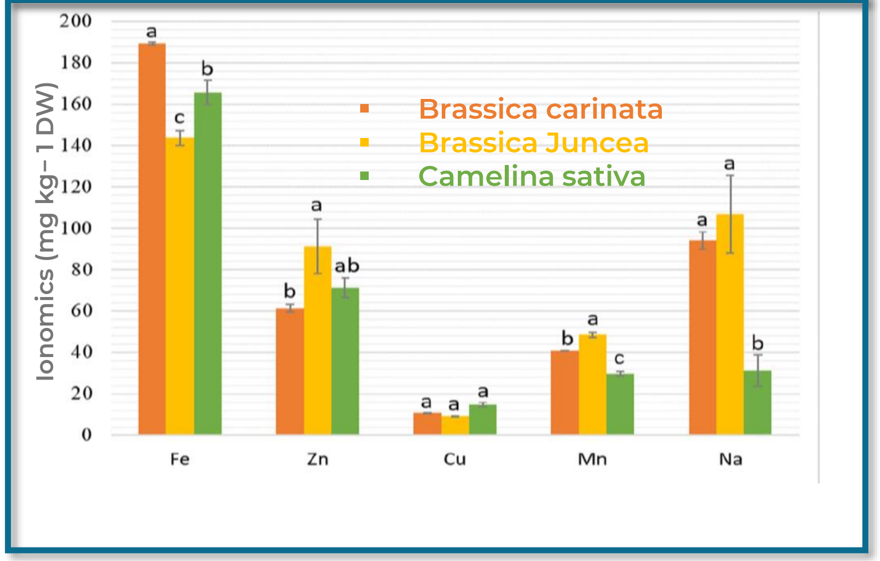
Oil-seed cakes valorisation: characterization

Brassica carinata, Brassica juncea, Camelina sativa*



Bars depict means, error bars depict standard deviation. Means with the same letter are not statistically different (ANOVA, p < 0.05, Tukey test).



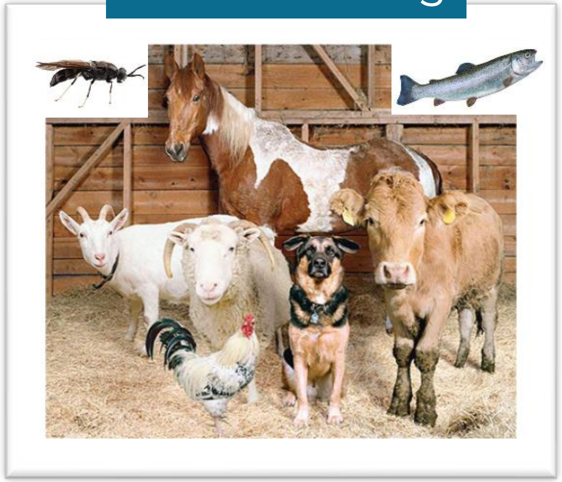


Ionomics (mg kg-1 DW) of defatted seed cakes.
Macroelement reported in the bottom box - microelement in the top one.
Bars depict means, error bars depict standard deviation. Means with the same letter are not statistically different (ANOVA, p < 0.05, Tukey test).

*Ceriani, M., D'Imporzano, G., De Nisi, P., Pilu, S., Pettinaroli, C., Gugliucci, W., Pasini, T., Rapone, I., Adani, F., 2024a. Oil cake recovery supports biofuel production sustainability from second-generation non-edible oil-crops. Bioresour Technol Rep 25, 101798.

Oil-seed cakes for animal feeding

Animal feeding



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Regulation contained the catalog of animal feeding raw materials

C. Sativa *B. Juncea* *B. Carinata* *Gossypium L.*,




H. Annuus *C. Tinctorius* *A. Hypogaea*



Formulation of feeding diet with oil seed cake as protein source cake for different animal species

Drawbacks

Erucic acid content : 7 mg/kg body weight (bw) per day

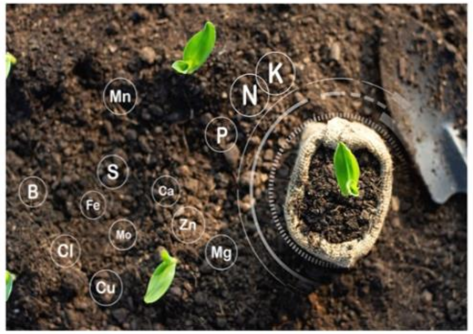
Glucosinolates content : 30 mmol/kg body weight (bw) per day

ACTIVITIES

R&D Eni	Stakeholder	
Physic-chemical characterization of different cakes	In vitro digestibility test In vivo test	Test of cake use in animal feeding

Oil-seed cakes for fertilizers

Fertilizers



Regulation (EU) 2019/1009 concerning EU fertilising products

SOIL ORGANIC CARBON

Formulation of organic fertilizer with oil seed cake as nitrogen source cake for different crops

Key points

Maximum application of oil-seed cake in soil (ton per ha)

Fumigant action

Nitrate leaching reduction

ACTIVITIES

R&D Eni	Stakeholder	
Plant germination in small growth chamber	Bio-enrichment of cake as plant bio-stimulant and fumigant	Cake optimal concentration
Plant growth and production in walk-in chambers		Application of optimal cake concentration on open field and greenhouse
Scale-up on field trial		

Oil-seed cakes for biochar production

Biochar: a strategy for the valorisation of residual and waste biomass

FEEDSTOCK	PROCESS	PRODUCTS
Agro-forestry waste and residues Agro-industrial waste and residues (e.g. cakes) Other ligno-cellulosic waste and residues	Pretreatment (e.g. drying, grinding) ↓ Slow Pyrolysis	**Biochar** **Biochar is the main product of slow pyrolysis** The secondary product consists of a gaseous stream (condensable and non-condensable) that can be used to provide thermal energy to the pyrolysis process (endothermic)

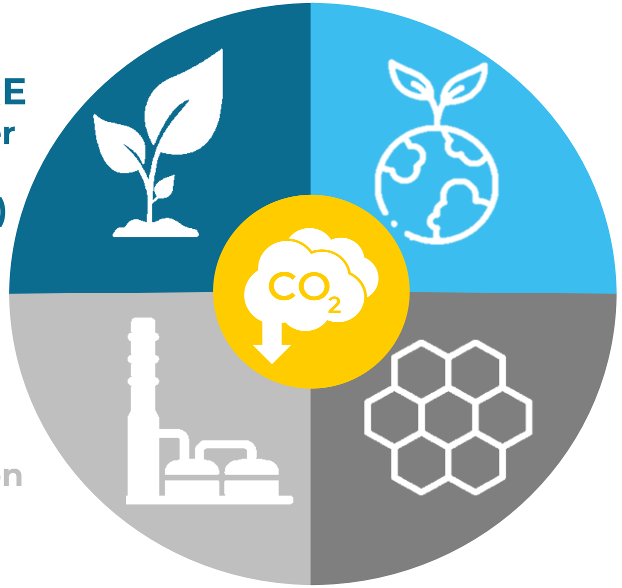
PROPERTIES OF BIOCHAR

Biochar is characterized by the following physicochemical properties:

- ❑ High **organic carbon content** (60-85%) with high **stability in the soil** (>100 years) → **Carbon stock material**
- ❑ **Porous structure** with high surface area
- ❑ **Retention of water, nutrients, contaminants**
- ❑ Good **calorific value** (HHV = 20-30 MJ/kg)
- ❑ **Ion exchange** capacity

Biochar is a multifunctional material suitable for fields of application of interest to Eni

FIELDS OF APPLICATION OF BIOCHAR



AGRICULTURE
- Soil improver of the soil (Energy crops)

PROCESSES ENVIRONMENTAL
- Soil remediation
- Water treatment

PROCESSES INDUSTRIAL
- Gas purification
- Digestion Anaerobic

SCIENCE OF MATERIALS
- Building
- Battery
- Catalysts

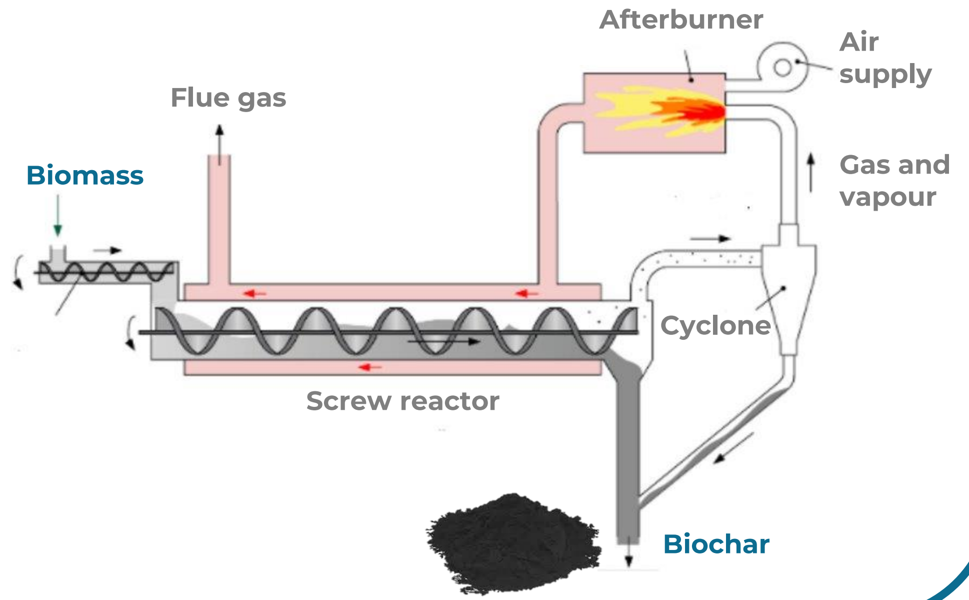
CARBON STOCK

Biochar production – Thermochemical process

Among all the thermochemical process the **slow pyrolysis** was chosen as reference technology because it aims at **maximizing the yield in biochar**

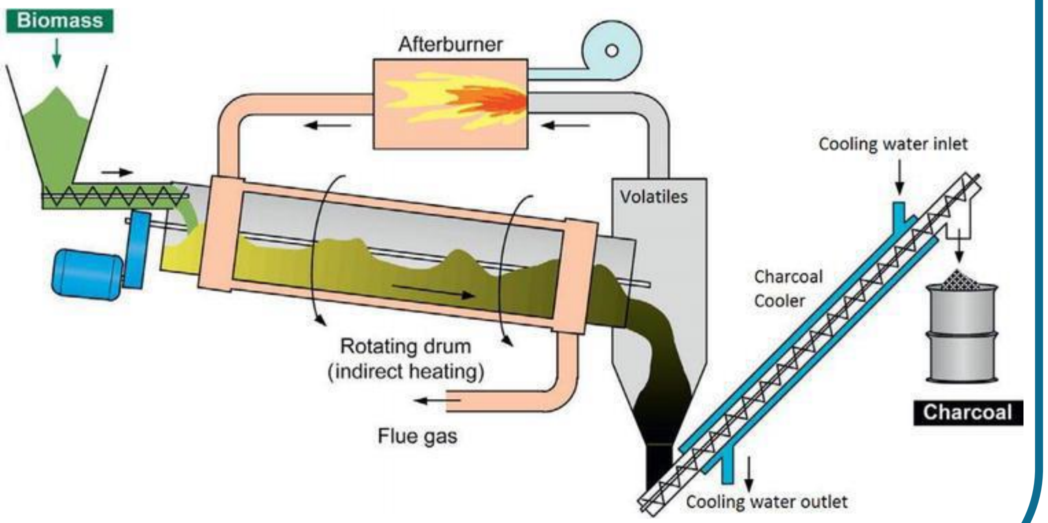
- ❑ Long residence time
- ❑ Temperature range: 400-700°C
- ❑ Oxygen free conditions

Auger



- ❑ **Uniform residence time**
- ❑ **Good control of biochar quality**

Rotary kiln



- ❑ **Simplified design (easier scale-up)**
- ❑ **Lower costs**

Biochar production – R&D tests (Lab-scale)

Feedstock

Cakes produced in R&D press machines:

- ❑ Camelina Sativa
- ❑ Hevea Brasiliensis
- ❑ Brassica Juncea
- ❑ Cartamo

Operating conditions

Slow pyrolysis runs:

- ❑ Biomass loaded = 150 g
- ❑ Pressure = 1 atm
- ❑ Temperature = 400-700 °C
- ❑ T-ramp = 10 °C/min
- ❑ Oxygen-free conditions (Q_{N2}=1.5 Nl/min)

Cake

Batch reactor

Biochar

Co-products:

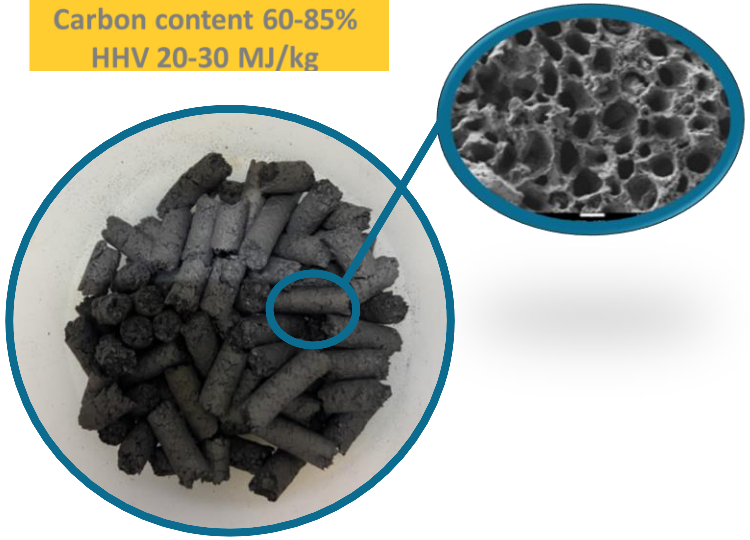
- ❑ Bio-oil
- ❑ Syngas

Biochar production - R&D tests (Pilot-scale)

Cake

Slow pyrolysis pilot reactor

Carbon content 60-85%
HHV 20-30 MJ/kg



Biochar

Key points

Biochar characterization: H/C and C/N ratio, C_{org}, pH, porosity, ash, PAH

Soil characteristics

Maximum application of biochar in soil (ton per ha)

Slow Pyrolysis

- Oxygen-free conditions
- Long residence time (min-hours)
- T=400-700°C
- Biochar yield = 30-40% w/w

Thermochemical process aim at maximizing the yield in biochar

Biochar properties

- Micro-porous structure
- High surface area
- High water-holding capacity
- Ion exchange capacity
- Nutrient capacity
- Contaminant sorbtion capacity
- High stability in soil (> 100yr)
- Carbon sink

Biochar production - Results

TESTED BIO-FEEDSTOCKES

As feedstock we have selected **different residual press-cakes** from mechanical extraction of various oleaginous seeds.

Cakes derived from the following sources:

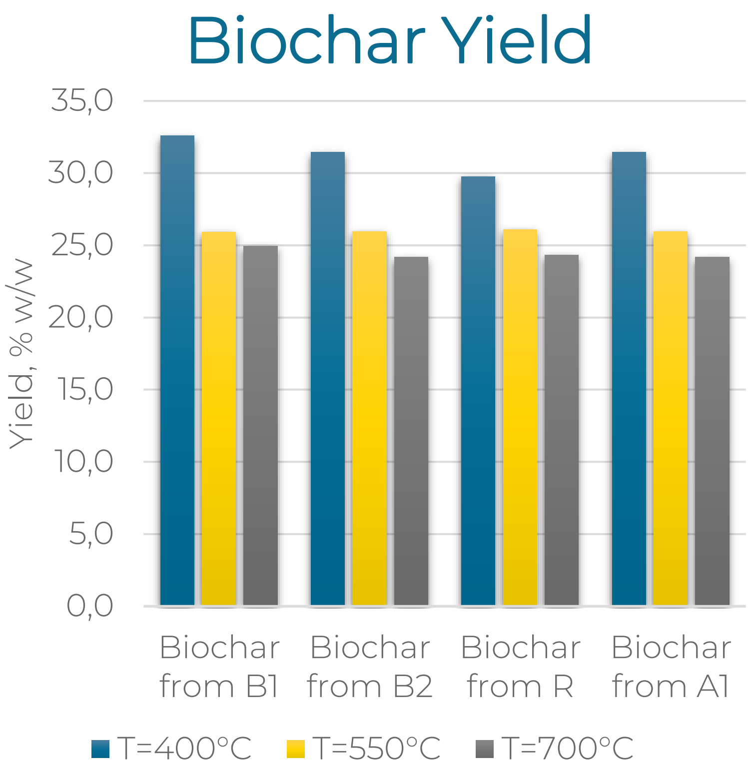
- ❑ Asteracea 1 (“A1”)
- ❑ Agri-supply chain residuals (“R”)
- ❑ Brassicacea 1 (“B1”)
- ❑ Brassicacea 2(“B2”)

SLOW PYROLYSIS RUNS FOR BIOCHAR PRODUCTION

Slow pyrolysis was chosen as reference technology because it allows to maximize the biochar production.

Operating conditions (semi-batch lab-scale plant):

- ❑ Biomass loaded = 150 g
- ❑ Temperature = 400-550-700 °C
- ❑ Oxygen-free conditions (Q_{N2}=1,5 Nl/min)
- ❑ Pressure = 1 atm



The slow pyrolysis conditions had guaranteed a good biochar yield ranging from 25-35% and favored by low temperature.

Biochar production - Results

The biochar was characterized following a dedicated characterization protocol. For soil amendment application, biochar must be compliant with fertilizers regulations (i.e. EU Regulation 2019/1009, D. Lgs. n°75 2010 ITA).

Tipo:	BIOCHAR from B 1			BIOCHAR from R			BIOCHAR from B 2			BIOCHAR from A 1		
T:	400°C	550°C	700°C	400°C	550°C	700°C	400°C	550°C	700°C	400°C	550°C	700°C
C tot (% d)	59,3	67,4	67,7	72,9	79,7	79,4	65,3	66,7	68,2	70,2	74,0	73,4
C org (% d)	59,3	66,2	67,6	71,9	79,1	79,4	58,4	64,0	67,8	69,6	73,0	73,4
C inorg (% d)	ND	1,2	0,1	1,1	0,7	ND	1,9	2,7	0,3	0,6	1,0	ND
H (% d)	3,2	2,1	1,1	3,5	2,2	1,1	3,6	1,9	1,0	3,6	2,2	1,1
N (% d)	7,5	7,6	6,5	3,3	3,1	2,7	7,8	7,1	6,5	5,1	4,6	4,0
S (% d)	0,9	0,4	0,6	<0,2	<0,2	<0,2	1,3	0,9	0,8	0,3	0,2	<0,2
O (% d)	14,5	6,1	6,5	6,7	7,5	2,9	11,2	17,5	5,2	11,1	11,5	8,7
Ash (% d)	14,7	16,5	17,6	6,7	7,5	13,9	13,7	17,6	18,3	9,9	11,6	12,7
H/C (-, mol/mol)	0,6	0,4	0,2	0,6	0,3	0,2	0,7	0,4	0,2	0,6	0,4	0,2
C/N (-, mol/mol)	9,3	10,4	12,2	23,9	28,2	34,2	9,1	10,2	12,2	16,2	18,8	21,3

- ❑ Bulk parameters: water content, ashes content, pH, conductivity.
- ❑ Quantitative analysis: organic elemental analysis CHNS (H/C and C/N ratios), carbon speciation (organic and inorganic C, labile and stable carbon), organic pollutants (PAHs), inorganic macro and microelements.
- ❑ Physical analysis: granulometry, bulk density, porosity.

Biochar properties are influenced by feedstock source and pyrolysis conditions.

- ❑ The carbon is predominantly organic and is more abundant at higher temperatures.
- ❑ H/C ratios indicate that the organic carbon is stable and compliant with the legal limit (<0,7 mol/mol).
- ❑ Biochar from R shows higher C/N ratios, thus indicating a slower release of nitrogen in soil.
- ❑ The ash content places the samples in Class 1 (<10%wt) and 2 (from 10 to 40%wt).
- ❑ The polycyclic aromatic hydrocarbons (PAHs) are below the legal limit (<6 ppm).

Oil-seed cakes for biogas production

Cake

Anaerobic digestion (AD)

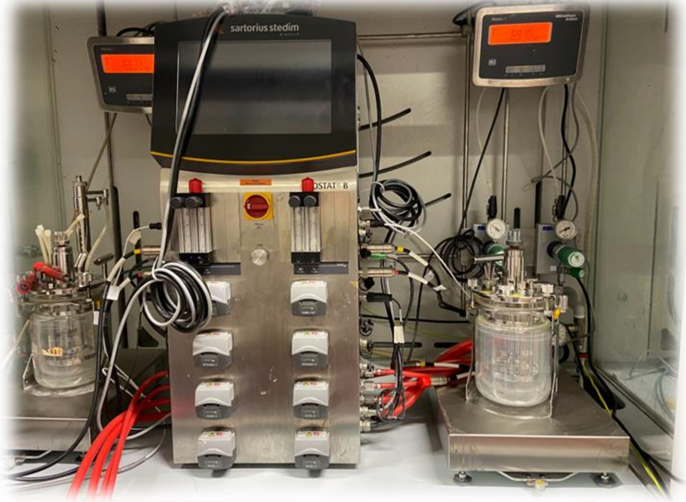
Electricity

District heating

Gas network / Transport

Biomethane

Laboratory equipment



- ❑ Batch and continuous testing
- ❑ Optimization of process conditions
- ❑ Comparison between conventional feedstocks (e.g. corn silage) and cakes
- ❑ Biochemical Metagenic Potential (BMP) determination
- ❑ Co-feeding in AD to respect a correct diet
- ❑ Regulatory aspects

Conclusions

- Biofuels will play a central role in achieving Eni's decarbonization mission by 2050.
- A key aspect is to supply raw materials for biorefineries from land that does not compete with the food supply chain and with processes in line with the strictest European standards.
- The agri-feedstock project, which envisages the production of oils from oil seeds, is just one piece of our energy transition road. Eni's biorefineries, which are used to transform biological raw materials into biofuels, are also fueled by waste raw materials from used cooking oil, animal fats and other biomass.
- R&D activities are focus on testing different agri-feedstocks, maximizing oil extraction and increasing the environmental and economic sustainability of the supply chain by valorizing all agricultural production residues and waste.
- Multidisciplinary approach: combination of knowledge and skills from several academic disciplines (e.g. agronomist, industrial chemist, engineer, biotechnologist, physicist, …) to address complex issues and difficulties.

THANK YOU FOR YOUR KIND ATTENTION

Q&A